of tetracycline by twenty-fold or greater are 2-carboxamide to nitrile, epimerization at C.4, epimerization at C.5a, and dehydrogenation at C.5a(11a).

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STUDIES[1] INVOLVING ISOTOPICALLY LABELLED FORMIC ACID AND ITS DERIVATIVES. IV. DETECTION OF CYANIDE (CN^-) IN A MIXTURE OF FORMIC ACID AND NITROGEN IN THE MASS SPECTROMETER

Sir:

During mass spectrometric studies of formic acid,[1] a research spectrometer[2] was modified for examining ion-molecule reactions. An essentially field-free region was set up between the ionization chamber and the first accelerating plate. Ions produced from one gas in the ionization chamber are passed at low energy through neutral molecules of another gas introduced into the field-free space. As the 10-fold higher pressure[3] in the chamber permits little back diffusion from the field-free region, it is possible to determine which of two species furnishes the ion in an ion-molecule reaction by inverting the mode of addition of two gases and noting the effect on the relative abundance of a production.

Ionization of formic acid in the chamber by electrons having an indicated energy[4] of 2.3 e.v. produced $HCOO^-$ ions[1] and essentially no positive ions.[5]

With nitrogen gas in the field-free region, a negative ion of mass 26 was detected. Its mass was not affected by substitution of DCOOH for the formic acid. Substitution of either $HC^{13}OOH$ for formic acid or nitrogen-N^{15} for nitrogen shifted the mass of this ion to 27. Use of both $HC^{13}OOH$ and nitrogen-N^{15} in the same experiment caused mass 28 to appear. When carbon monoxide or carbon dioxide was substituted for formic acid the ion of mass 26 failed to appear. We conclude that this negative ion is CN^-. Since the positive peaks known to arise from hydrogen cyanide and cyanogen[6] were absent even with the electron energy raised to 75 e.v., neither of these substances is a likely precursor. Inversion of the mode of addition—that is introduction of nitrogen into the ionization chamber and formic acid into the field-free region—resulted in a 10-fold reduction in abundance of the CN^- ion.

When, in a subsequent experiment, an equimolar mixture of nitrogen and formic acid at 2 mm. pressure was subjected to a spark discharge, 1% hydrogen cyanide was found in the product mixture.

In the mass spectrometric study, some active species produced from formic acid in the ionization chamber apparently reacts with nitrogen molecules to give rise to the CN^- ions. The active species is probably the negative ion,[7] $HCOO^-$, although we cannot rule out all other possibilities. Were the present reaction between $HCOO^-$ and N_2 molecules, this would presumably be the first mass-spectrometric observation of a negative[8] ion-molecule reaction of this type.

The present results indicate some similarity between the reactions produced by the electric discharge and those effected by the 2.3 e.v. electrons in the mass spectrometer. The results also may be significant because of a current interest in nitrogen fixation by ionizing radiations.

Helpful discussions with Russell Baldock, John Burns and P. S. Rudolph are acknowledged.

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[1] Previous study, G. A. Ropp and C. E. Melton, THIS JOURNAL, **80**, 3509 (1958).

[2] C. E. Melton, G. A. Ropp and P. S. Rudolph, *J. Chem. Phys.*, in press (October, 1958).

[3] G. F. Wells and C. E. Melton, *Rev. Sci. Instr.*, **28**, 1065 (1957).

[4] C. E. Melton and G. F. Wells, *J. Chem. Phys.*, **27**, 1132 (1957); previous experience indicates that the actual electron energy does not differ by more than ±3 e.v. from the indicated energy.

[5] T. Mariner and W. Bleakney, *Phys. Rev.*, **72**, 792 (1947).

[6] C. A. McDowell and J. W. Warren, *Trans. Faraday Soc.*, **48**, 1084 (1952); K. E. Dorsch and H. Kallman, *Z. physik.*, **60**, 376 (1930); J. T. Tate, P. T. Smith and A. L. Vaughan, *Phys. Rev.*, **48**, 525 (1935).

[7] The low energy of the ionizing electrons makes it improbable that a positive ion is the precursor of the CN^- ion. A free-radical precursor is unlikely at the low pressures employed since a three-step process would be required: (a) electron impact with formic acid to produce a radical, (b) reaction of the radical with nitrogen, and (c) conversion of the resulting species to CN^-.

[8] A number of positive ion-molecule reactions are known: see H. S. Johnston in *Annual Reviews of Physical Chemistry*, **8**, 252–3 (1957). However, see E. E. Muschlitz, Jr., *J. Appl. Phys.*, **28**, 1414 (1957).

[9] Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

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RECEIVED JULY 25, 1958

A NOVEL SYNTHESIS OF METAL CARBONYLS USING TRIETHYLALUMINUM AS THE REDUCING AGENT[1]

Sir:

We wish to report a novel method for preparing transition metal carbonyls, one that is of particular value for the less accessible metal carbonyls. The method consists essentially of a reductive carbonylation[2] reaction of an appropriate salt of the transition metal with triethylaluminum and carbon monoxide. The reaction generally is carried out in an ether solvent at elevated temperature and pressure. The triethylaluminum appears to function in this reaction as a selective reducing agent for the transition metal, permitting carbonylation to occur at a rate greater than the rate of reduction to the free metal.

The method differs from the conventional Grignard methods[3–7] in that (1) it is applicable to the

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[1] Reductive Carbonylation Synthesis of Metal Carbonyls. I.

[2] The term "reductive carbonylation" as used here denotes overall reduction and carbonylation of the transition metal in a compound or intermediate in which the metal has a formal positive charge of one or greater.

[3] A. Job and A. Cassal, *Compt. rend.*, **183**, 392–4 (1926).

[4] A. Job and J. Rouvillois, *Bull. soc. chim.*, **41**, 1041 (1927).

[5] W. Hieber and E. Romberg, *Z. anorg. Chem.*, **221**, 321 (1935).

[6] K. A. Kocheskov, A. N. Nesmeyanov, N. M. Nadj, I. M. Rossinskaya and L. M. Borissova, *Compt. rend. acad. sci.*, **26**, 54 (1940).

[7] B. B. Owen, J. English, Jr., H. G. Cassidy and C. V. Dundon, THIS JOURNAL, **69**, 1723 (1947).