A Nondegradative Reaction of Active Nitrogen. Conversion of Ethanol to Acetamide

Sir:

We have previously reported[1] the interception of HCN precursor(s) in the reaction of active nitrogen with methanol in aqueous solution. In this work it was shown that tetranitromethane suppresses formation of HCN from methanol, ethanol, isopropyl alcohol, and *tert*-butyl alcohol. In the case of methanol, the decrease in yield of HCN associated with the presence of tetranitromethane is accompanied by an equimolar increase in the yield of ethylene glycol. No carbonaceous nitrogenous product other than HCN was found in the previous work with methanol. We now find that the major nitrogenous product of the reaction of aqueous active nitrogen with ethanol is acetamide. *This appears to be the first reported case of efficient nondegradative incorporation of nitrogen into an organic molecule resulting from reaction with active nitrogen.*[2] Smaller yields of amides have also been obtained from methanol and isopropyl alcohol.

Experimental procedures were the same as those which were reported previously.[1] Acetamide was isolated by evaporating the combined solutions from four 20-min runs employing 5 *M* ethanol, first in a rotary evaporator under reduced pressure at 31–35° and then to dryness over P_2O_5 in a vacuum desiccator. The solid product was recrystallized once from $HCCl_3$–*n*-hexane and identified as acetamide by the absence of any depression in its mixture melting point with an authentic sample and by the identity of its infrared spectrum in chloroform solution with that of the authentic material. Quantitative yields of acetamide were determined by the method of Robertson, *et al.*,[3] which involves formation of the hydroxamic acid at steam-bath temperature and measurement of optical absorption due to the Fe^{III} complex of the latter. This method does not distinguish between acetamide and ethyl acetate. Ethyl acetate would have been removed during the isolation and recrystallization of acetamide. It was therefore shown that reacted solutions respond to the method of Goldenberg[4] in exactly the same way as does acetamide and are substantially less reactive than ethyl acetate. In this method, the hydroxamic acid is generated at room temperature and is formed much more slowly by amides than by esters.

With an incident N(^{4}S) flow rate[5] of 50×10^{-8} mol sec^{-1}, product yields from the reaction of 1–10 *M* aqueous solutions of ethanol for 5 min were (in units of 10^{-8} mol sec^{-1}): HCN,[6] 19; CH_3CONH_2,[3] 29; NH_3,[7] 3; NH_2NH_2,[8] <0.1; CH_3CHO,[9] 6.5. Thus, about 60% of incident N(^{4}S) is fixed as acetamide while most of the balance appears in HCN. Reaction of 1–5 *M* aqueous ethanol saturated with tetranitromethane ($1.0–1.5 \times 10^{-2}$ *M*) with 50×10^{-8} mol sec^{-1} of active nitrogen for 5 min gave no detectable HCN,[6] *i.e.*, less than 0.2×10^{-8} mol sec^{-1}. Other yields (in units of 10^{-8} mol sec^{-1}) were: "CH_3CONH_2,"[3] 7 (sum of amide and ethyl acetate); NH_3,[7] 1; CH_3CHO,[9] 44; $HC(NO_2)_3$,[10] 19. Under identical conditions, except that the discharge was not running, the yields of "CH_3CONH_2," CH_3CHO, and $HC(NO_2)_3$ from 5 *M* EtOH were 5, 7, and 0.7, respectively. The data obtained in the presence of TNM can be interpreted as indicating that precursors of HCN and acetamide are intercepted by tetranitromethane. It is proposed that a key precursor of both these products is the $CH_3CH(OH)\dot{N}H$ radical.

The generality of such nondegradative incorporation of nitrogen into organic molecules is under investigation. Preliminary data indicate that little nitrogen, no more than 2%, is fixed as formamide[3] in the reaction of CH_3OH with active nitrogen. However, with isopropyl alcohol ~30% of incident N is fixed as amide nitrogen,[3] presumably in acetamide and/or *N*-methylacetamide.

Acknowledgment. We wish to acknowledge support of this research by the National Science Foundation under Grant No. GP 8186.

C. T. Chen, N. N. Lichtin*
Department of Chemistry, Boston University
Boston, Massachusetts 02215
Received August 18, 1971

(1) C. T. Chen and N. N. Lichtin, *J. Amer. Chem. Soc.*, **92**, 7506 (1970).
(2) In the gas phase the reaction of ethanol with active nitrogen gives HCN, H_2O, and H_2 as the main products along with small amounts of C_2H_6, C_2H_4, CH_4, CH_3CN, C_2N_2, CO, and CH_3CHO. See P. A. Gartaganis, *Can. J. Chem.*, **43**, 935 (1965).
(3) E. B. Robertson, B. D. Sykes, and H. B. Dunford, *Anal. Biochem.*, **9**, 158 (1964).
(4) V. Goldenberg, *Anal. Chem.*, 30, 1327 (1958).
(5) Determined by NO titration.
(6) J. M. Kruse and M. G. Mellon, *Anal. Chem.*, **25**, 446 (1953).
(7) A. Matsumoto, N. Hayashi, and N. N. Lichtin, *Radiat. Res.*, **41**, 299 (1970).
(8) G. W. Watt and J. D. Chrisp, *Anal. Chem.*, **24**, 2006 (1952).
(9) E. Stotz, *J. Biol. Chem.*, **148**, 585 (1943).
(10) B. H. J. Bielski and A. O. Allen, *J. Phys. Chem.*, **71** 4544 (1967).

Carbon-13 Nuclear Magnetic Resonance of Some Group VIb Metal Carbonyls and Derivatives[1]

Sir:

While application of carbon-13 nuclear magnetic resonance (cmr) to problems of organic chemistry is now becoming routine, few spectra of metal carbonyls or organotransition metal complexes have been reported.[2–5] Considering the current interest in cmr, studies to determine factors which influence carbonyl chemical shifts are needed, especially in view of contention in the literature with regard to the use of carbonyl stretching frequencies, force constants and band intensities,[6] and proton[5] and ^{31}P coupling constants and chemical shifts[6–8] in efforts to assess inductive (σ) and mesomeric (π) effects of a ligand (L) on metal–carbonyl bonding. Accordingly, cmr spectra of the three group VIb metal carbonyls $M(CO)_6$ (M = Cr,

(1) Presented in part at the 3rd *Inorganica Chimica Acta* Symposium, Venice, Italy, Sept 1970, and the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.
(2) O. A. Gansow and B. Y. Kimura, *Chem. Commun.*, 1621 (1970).
(3) R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962); *J. Chem. Soc. A*, 861 (1967).
(4) H. L. Retkofsky, E. N. Frankel, and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **88**, 2710 (1966).
(5) P. C. Lauterbur and R. B. King, *ibid.*, **87**, 3266 (1965).
(6) For a recent succinct review containing appropriate references, see S. O. Grim and D. A. Wheatland, *Inorg. Chem.*, **8**, 1716 (1969).
(7) F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 1916 (1970); R. T. Bertrand, F. C. Ogilvie, and J. G. Verkade, *ibid.*, **92**, 1908 (1970); R. L. Keiter and J. G. Verkade, *Inorg. Chem.*, **8**, 2115 (1969), and references cited therein.
(8) G. G. Mather and A. Pidcock, *J. Chem. Soc. A*, 1226 (1970).