The C–N Bond Dissociation Energy in Nitrosyl Cyanide

By **Brian G. Gowenlock,* Christopher A. F. Johnson, Colin M. Keary,** and **Josef Pfab,** Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh EH14 4AS

D(NC–NO) has been determined by an electron impact method. The value obtained is 28·8 ± 2·5 kcal mol^{-1} (120·5 ± 11·5 kJ mol^{-1}). This value is compared with those obtained for other nitroso-compounds and it is concluded that there is no simple relation between C–N bond dissociation energy and bond length in these compounds, the predominant contribution to the bond dissociation energy being the reorganisation energy in the liberated nitric oxide.

THE compound nitrosyl cyanide has recently been isolated and some details of its molecular structure have been published.[1] It was of interest to measure *D*(NC–NO) in order to confirm our previous predictions [2,3] that the governing factor in this value is the reorganisation energy of the liberated nitric oxide and that there is no correlation between the bond dissociation energy and the bond length. Nitrosyl cyanide provides a good test of this hypothesis because of the marked shortening of the central C–N bond compared with nitrosomethane [4] and other *C*-nitroso-compounds, there being only one [5] shorter C–N bond in a *C*-nitroso-compound.

EXPERIMENTAL

Nitrosyl cyanide was prepared by the method of Dickinson *et al.*[1] It was redistilled until mass spectroscopic investigation showed it to be free from nitrosyl chloride. It was stored at liquid nitrogen temperature with exclusion of light. The mass spectrum of nitrosyl cyanide at 70 eV was measured (see Table). The appearance potential of the NO^+ ion was measured by the energy distribution difference method as before.[2,3] The value obtained is 10·5 ± 0·1 eV. The derived value for *D*(NC–NO) is therefore 1·25 ± 0·12 eV (120·5 ± 11·5 kJ mol^{-1}; 28·8 ± 2·5 kcal mol^{-1}). This value is an upper limit, because the fragments may contain an excess of kinetic and other excitation energy.

Mass spectrum of NO·CN at 70 eV

m/e	30	28	27	26	44	52
Relative intensity	100	61·2	20·4	8·8	16·3	16·3

DISCUSSION

It is of interest to note that the C–N bond in nitrosyl cyanide is the weakest yet measured for any *C*-nitroso-compound. A survey of the literature indicates that *r*(C–X) is always shorter in NC–X than in H_3C–X for the cases X = H, CH_3, Cl, Br, I, NH_2, and NO and this is usually associated with the effect of *sp* hybridisation at carbon compared with sp^3 hybridisation. It is instructive to notice that with the exception of X = NO, there is a strengthening of *D*(C–X) on passing from CH_3 to CN and this is generally of the order 20—40 kcal mol^{-1} (80—160 kJ mol^{-1}). We have previously noted that $D(\text{X–NH}_2) - D(\text{X–NO})$ is much larger for carbon and hydrogen nitroso-compounds than for halogen, oxygen, and nitrogen nitroso-compounds. It is unfortunate that there is no direct determination of the heat of formation of cyanamide, but use of the values calculated by Radom *et al.*[6] in conjunction with the heats of formation of the radicals listed by Benson [7] gives $D(\text{NC–NH}_2) - D(\text{NC–NO})$ = 88—97 kcal mol^{-1} (369·6—407·4 kJ mol^{-1}), much greater than the 40—54 kcal mol^{-1} values which were obtained for other nitroso-compounds.[3] This also implies a considerable reorganisation energy of the nitric oxide liberated on fission of the NC–NO bond.

It is instructive to compare the molecules nitrosyl cyanide and trifluoronitrosomethane which are the two *C*-nitroso-compounds possessing the weakest C–N bonds (29 and 31 kcal mol^{-1} respectively). It should be noted, however, that in nitrosyl cyanide the C–N bond is short [1] (1·401 Å) whereas in trifluoronitrosomethane it is long [8] (1·555 Å). This emphasises that in these molecules no immediate correlation is to be found between bond dissociation energy and bond length.

We acknowledge helpful discussion with Dr. J. K. Tyler concerning the preparation of nitrosyl cyanide. C. M. K. acknowledges receipt of an S.R.C. maintenance allowance.

[4/1869 *Received*, 12*th September*, 1974]

---

[1] R. Dickinson, G. W. Kirby, J. G. Sweeny, and J. K. Tyler, *J.C.S. Chem. Comm.*, 1973, 241.

[2] P. J. Carmichael, B. G. Gowenlock, and C. A. F. Johnson, *Internat. J. Chem. Kinetics*, 1972, **4**, 339.

[3] P. J. Carmichael, B. G. Gowenlock, and C. A. F. Johnson, *J.C.S. Perkin II*, 1973, 1853.

[4] D. Coffey, C. O. Britt, and J. E. Boggs, *J. Chem. Phys.*, 1968, **49**, 591.

[5] M. S. Webster, *J. Chem. Soc.*, 1956, 2841.

[6] L. Radom, W. J. Hehre, and J. A. Pople, *J. Chem. Soc.* (*A*), 1971, 2299.

[7] S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1968.

[8] M. I. Davis, J. E. Boggs, D. Coffey, and H. P. Hanson, *J. Phys. Chem.*, 1965, **69**, 3727.