C–N Bond Dissociation Energies in Some Halogenated *C*-Nitroso-compounds and in Di-t-Butyl Nitroxide

By **Peter J. Carmichael, Brian G. Gowenlock,*** and **Christopher A. F. Johnson,** Department of Chemistry Heriot–Watt University, Edinburgh EH1 1HX

Measurements of the R–NO bond dissociation energy in some halogenated *C*-nitroso-compounds and in di-t-butyl nitroxide have been made using an electron impact method. The values obtained are: 31 kcal mol^{-1} for $D(CF_3–NO)$, 32 for $D(CCl_3–NO)$, 62 for $D(C_6F_5–NO)$, and 29 for $D(Bu^tNO–Bu^t)$. These values are compared with bond dissociation energies in a range of other nitroso-compounds, and general relationships between structural parameters and bond dissociation energies are discussed. The anomalous value for $D(C_6F_5–NO)$ is discussed.

IN a recent paper[1] we presented values for D(C–N) in nitrosobenzene, 2-methyl-2-nitrosopropane, 2-nitrosopropane, and 2-methyl-2-nitrosobutane determined by appearance potential methods. These were the first direct measurements of D(C–N) in *C*-nitroso-compounds. It appeared of interest to extend these studies to halogenated nitroso-compounds in order to consider general relationships between structural parameters and bond dissociation energies.

EXPERIMENTAL

Trifluoronitrosomethane and pentafluoronitrosobenzene were commercial samples (Fluorochem. Ltd.). Both were purified by vacuum distillation before use. A pure sample of trichloronitrosomethane was made available by Dr. H. Sutcliffe. It was stored in the dark at liquid nitrogen temperature and vacuum distilled before use. A highly purified sample of di-t-butyl nitroxide was provided by Dr. A. R. Forrester. 2-Methyl-2-nitrosopropane was prepared as in ref. 1. Mass spectra at 70 eV and appearance potentials were measured using an AEI MS10 mass spectrometer using the techniques detailed previously.[1]

When molecular ionization potentials were required they were measured using a Perkin-Elmer PS18 photoelectron spectrometer. (We are indebted to Professor E. A. V. Ebsworth for these measurements.)

RESULTS AND DISCUSSION

The mass spectra of the four molecules studied are given in Table 1. Comparison with literature data is possible in two cases.[2,3] Dubov and Khokhlova's results [2] for trifluoronitrosomethane (measured at 40 eV) show that the four most prominent ions correspond to NO^+, CF_3^+, CF_2^+, and CF^+. Our data (70 eV) are in agreement with this order. In the case of trichloronitrosomethane, our results (70 eV) compare favourably with those of Briden *et al.*[3] (50 eV) the only significant difference being in the much larger peak observed by us at *m*/*e* 61, presumably due to the $ClCN^+$ ion. Appearance potentials are presented in Table 2, together with the ionization potential values of the appropriate fragments and the D(C–N) values derived thereby. It is necessary to comment upon the procedure adopted for determining the bond dissociation energies for each of the molecules studied. In the case of trifluoronitrosomethane, the application of Stevenson's rule[4] implies that it is necessary to base the calculation of D(C–N) upon the appearance potential of the nitric oxide ion. Use of the appearance potential of the trifluoromethyl radical ion, in conjunction with the appropriate ionization potential produces virtually the same value for D(C–N). In contrast for trichloronitrosomethane, the fragment of lower ionization potential is clearly the trichloromethyl radical. In the case of pentafluoronitrosobenzene it was impossible to make an accurate measurement of the appearance potential of the pentafluorophenyl radical ion, the ionization curves obtained either by the semi log plot or by the energy distribution difference method giving curvilinear plots at acute angles to the calibration ionization current. This is, however, of no consequence

TABLE 1

Mass spectra measured at 70 eV

Trichloronitrosomethane, CCl_3NO

m/*e*	117	119	30	112	61	47	114	82	121
Relative intensity	100	92	80	78	69	55	52	37	34

Trifluoronitrosomethane, CF_3NO

m/*e*	30	69	50	31	20	99	12	45
Relative intensity	100	50	11	6	4	3	2	2

Pentafluoronitrosobenzene, C_6F_5NO

m/*e*	30	31	20	112	93	95	167
Relative intensity	100	20	15	12	7	3	2

Di-t-butyl nitroxide, $C_8H_{18}NO$

m/*e*	41	57	29	39	27	56	15	42	43	30
Relative intensity	100	90	53	33	32	24	21	15	14	10

TABLE 2

Appearance potentials (A.P.), ionisation potentials (I.P.), and derived D values

Compound	Molecular ion A.P./eV	Fragment A.P./eV	Fragment I.P./eV	D(C–N)/ kcal mol^{-1}
CF_3NO	10·41 ± 0·1 [a]	10·61 ± 0·1 [a,d]	9·23 [h]	31 ± 3
	10·44 ± 0·1 [b]	11·36 ± 0·1 [b,e]	10·1 [i]	
	10·40 ± 0·1 [c]	11·41 ± 0·1 [a,e]		
CCl_3NO		10·12 ± 0·1 [b,f]	8·78 [i]	32 ± 3
C_6F_5NO		11·93 ± 0·1 [a,d]	9·23 [h]	62 ± 5
		11·97 ± 0·1 [b,d]		
Bu_2^tNO	7·9 ± 0·1 [a,b]	8·7 ± 0·1 [b,g]	7·42 [i]	29 ± 3
		8·9 ± 0·1 [a,g]		
Bu^tNO	8·55 ± 0·1 [c]			

[a] Energy distribution difference method. [b] Semi-log method. [c] Photoelectron spectroscopy. [d] NO^+. [e] CF_3^+. [f] CCl_3^+. [g] Bu^{t+}. [h] K. F. Huber, *Helv. Phys. Acta*, 1961, **34**, 929. [i] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, and K. Draxl, Nat. Bur. Stand. Reference Data System NSRDS-NBS26, 1969.

---

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

[2] S. S. Dubov and A. M. Khokhlova, *Zhur. obschchei Khim.*, 1964, **34**, 1961.

[3] A. R. Briden, D. Price, and H. Sutcliffe, *J. Chem. Soc.* (*B*), 1968, 387.

[4] D. P. Stevenson, *Discuss. Faraday Soc.*, 1951, **10**, 35.

to the calculation of D(C–N) because the ionization potential of nitric oxide is much lower than that of the pentafluorophenyl radical. In the case of di-t-butyl nitroxide it was necessary to confirm that the ionization potential of 2-methyl-2-nitrosopropane was greater than the ionization potential of the t-butyl radical. This was shown to be the case (see Table 2).

We have drawn attention [1] to the fact that the carbon–nitrogen bond in nitrosoalkanes is much weaker than the corresponding bond in primary amines and have pointed out that this weakness is due in large measure to the reorganisation energy of the nitric oxide that is liberated on bond fission. The data available suggest that it is now possible to attempt a comprehensive theory of bond dissociation energies in these molecules. We suggest that it is necessary to consider the combined effect of several structural features in order to account satisfactorily for bond dissociation energies in *C*-nitroso-compounds. These features are (a) the C–N bond length, (b) the N–O bond length, and (c) hybridisation, lone pair, and CNO bond angle. It is not unreasonable to assume that in structurally similar molecules a marked lengthening of a particular bond in only one member of the series is associated with a weakening of the bond in that particular molecule. Inspection of Table 3 shows that there is one known example of a long C–N bond, namely trifluoronitrosomethane. This is associated with a low value for D(C–N). It is suggested [5] that there is a contribution from the ionic form (I) to the structure

$$\overset{-}{C}F_3 \quad \overset{+}{N}O \qquad \text{(I)}$$

of trifluoronitrosomethane. A survey of the literature indicates that extension of the C–N bond on perfluorination also occurs for trifluoronitromethane (r_{CN} 1·56 Å) [6] but that in perfluorotrimethylamine C–N lengthening does not occur (data for trifluoromethylamine are lacking). It is known that trichloronitromethane possesses a long C–N bond (r_{CN} 1·59 Å) [7] and it is tempting to assume that trichloronitrosomethane which has the same D(C–N) value as trifluoronitrosomethane will also have a long C–N bond. There is, however, at least one difficulty associated with this suggestion, namely the fact that the electron affinity of the trichloromethyl radical is considerably lower [8] than that of the trifluoromethyl radical, and consequently the contribution of the ionic structure analogous to (I) should be lower.

TABLE 3

Structural parameters for monomeric *C*-nitroso-compounds

Molecule	D(C–N)/ kcal mol^{-1}	r(CN)/ Å	r(NO)/ Å	ω(NO)/ cm^{-1}	$\widehat{CNO}$ (°)	Ref.
CH_3NO	(37—40)	1·49	1·22	1564	112·6	19, *a*
		1·480	1·213		113·2	*b*
CF_3NO	31	1·555	1·171	1595	121	5, *c*
CCl_3NO	32			1618		3
$Pr^{i}NO$	36·5					
$Bu^{t}NO$	34			1546		*a*
$C_5H_{11}{}^{t}NO$	36					
PhNO	41	1·44	1·24	1506	118	*a*, *d*
		1·47	1·21		116	
		1·51	1·17		114	
C_6F_5NO	62					
p-IC_6H_4NO		1·28	1·24	1488	125	*a*, *e*

[a] W. Lüttke, *Z. Elektrochem.*, 1957, **61**, 302. [b] A. P. Cox, personal communication. [c] J. Mason and J. Dunderdale, *J. Chem. Soc.*, 1956, 754. [d] Y. Hanyu and J. E. Boggs, *J. Chem. Phys.*, 1965, **43**, 3454. [e] M. S. Webster, *J. Chem. Soc.*, 1956, 2841.

It is also of interest to note that $D(CF_3\text{–}X) > D(CH_3\text{–}X)$ by *ca.* 1—3 kcal mol^{-1} where X = H, Cl, or Br and by a larger amount when X = alkyl.[9] It is apparent that the case for X = NO represents the only example where $D(CF_3\text{–}X) < D(CH_3\text{–}X)$.

The major anomaly in our D(C–N) values is pentafluoronitrosobenzene, the value being *ca.* 21 kcal mol^{-1} higher than for the non-fluorinated compound. Other physical properties of the two compounds show a marked similarity; in particular the electronic absorption spectrum in the visible [10,11] and the structures of the *cis*-dimeric forms.[12,13] It therefore seems probable that one or both of the fragments produced in the electron impact process $C_6F_5NO + e \longrightarrow C_6F_5 + NO^+ + 2e$ carries a considerable excess of energy.

In our previous paper [1] we drew attention to the importance of the electronic reorganisation energy in the NO fragment in accounting for the low values of D(C–N) in *C*-nitroso-compounds. We also compared the D(C–N) values in nitroso-, nitro-, and amino-compounds. We now extent these comparisons to the compounds studied in this paper and attempt a general understanding of bond dissociation energies D(X–NO), where X is hydrogen, alkyl, aryl, halogen, hydroxy, alkoxy, and dialkylamino, in terms of the hybridisation of the nitrogen atom and the nature of the lone pair electrons at the nitrogen atom. The available bond dissociation energy data are presented in Table 4. Column 4 of this Table presents a standard of comparison for X–N bond weakening in nitroso-compounds. There is little or no reorganisation energy associated with the change from a bonded amino-group (sp^3) to the free aminyl radical, and any change in X will be a constant feature in every comparison. We can therefore expect that any major differences in column 4 will reflect essential structural differences within the molecules concerned. It is immediately apparent that there are two groups of compounds exhibiting different patterns of bond dissociation energy variation, namely carbon and hydrogen nitroso-compounds on the one hand, and halogen, oxygen, and nitrogen compounds on the other. Ionic contributions may play some part

---

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

[6] I. L. Karle and J. Karle, *J. Chem. Phys.*, 1962, **36**, 1969.

[7] W. M. Barss, *J. Chem. Phys.*, 1957, **27**, 1260.

[8] F. M. Page and G. C. Goode, ' Negative Ions and the Magnetron,' Wiley-Interscience, London, 1969.

[9] E. Whittle, personal communication.

[10] G. M. Brooke, J. Burdon, and J. C. Tatlow, *Chem. and Ind.*, 1961, 832.

[11] W. J. Mijs, S. E. Hoekstra, R. M. Ulmann, and E. Havinga, *Rec. Trav. chim.*, 1958, **77**, 746.

[12] C. K. Prout, personal communication

[13] D. A. Dieterich, I. C. Paul, and D. Y. Cantin, *Chem. Comm.*, 1970, 1710.

in these energy differences, but we believe that the differences are not due primarily to ionic effects. It should be noted that for X = alkyl or hydrogen, the bond lengths r_{XN} are very similar for the molecules XNH_2 and XNO; for X = halogen, $r_{X-NO} > r_{X-NH_2}$; and for $X = Me_2N$, $r_{X-NO} < r_{X-NH_2}$.

TABLE 4

Intercomparison of C–N bond dissociation energies (all values in kcal mol^{-1})

X	$D(X-NH_2)$	D(X–NO)	$D(X-NH_2)$ − D(X–NO)
CH_3	80 [a]	(37—40) [e]	(40—43)
Pr^s	78 [a]	36·5 [e]	41·5
Bu^t	75 [a]	34 [e]	41
Ph	91 [a]	41 [e]	50
H	103 [a]	49 [f]	54
NMe_2	50 [b]	40·5 [b]	9·5
HO	59 [a]	49·5 [a]	9·5
OMe	48 [a]	39 [a]	9
F	64 [c]	57 [g]	7
Cl	60 [d]	38 [g]	22

[a] Derived from heats of formation of molecules given in S. W. Benson, F. R. Cruikshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279 and of fragments given in J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465. [b] As *a* with ΔH_f^0 NMe_2 obtained from I. P. Fisher and E. Henderson, *Trans. Faraday Soc.*, 1967, **63**, 1342. [c] Combination of data from P. Smith and C. N. R. Rao, *Canad. J. Chem.*, 1958, **36**, 1174 and J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465. [d] S. W. Benson, *J. Chem. Educ.*, 1965, **42**, 502. [e] Ref. 1. [f] M. J. Y. Clement and D. A. Ramsay, *Canad. J. Phys.*, 1961, **39**, 205 (see also note *g*). [g] Combination of data from 'JANAF Thermochemical Tables,' NSRDS-NBS37, U.S. Dept. of Commerce, Washington, 2nd. edn., 1971 and J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465.

There are other molecular properties which show similar differences to the bond dissociation energy differences, and this information is displayed in Table 5.

TABLE 5

X	$D(X-NH_2)$ − D(X–NO) kcal mol^{-1}	χ_{cc}(MHz) at nitrosyl nitrogen in XNO[14]	$-\sigma_p$(p.p.m.) for XNO [a]	$\lambda_{max.}$(nm) [11,a,b] for $n-\pi^*$(N) band
Ph	50		962	750
Me	[40—43]	5·52		680
Cl	22	3·8	695	475
NMe_2	9·5		595	361
HO	9·5	3·78(c) 3·55(t)		
OMe	9	3·47(c)	630	341
F	7	3·3	547	311

[a] L. O. Anderson, J. Mason, and W. van Bronswijk, *J. Chem. Soc. (A)*, 1970, 296. [b] P. Tarte, *Bull. Soc. chim. belges*, 1954, **63**, 525.

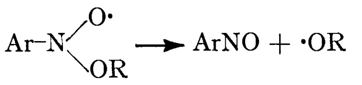
Cox *et al.*[14] have drawn attention to the fact that the quadrupole coupling constants at nitrogen in a number of XNO compounds can be correlated with the XNO angle, with the exception of nitrosomethane, suggesting that simple interpretations in terms of hybridisation changes alone are insufficient. We suggest that the information collected in Table 5 illustrates the importance of the changes in character of the lone pair electrons at the nitrogen atom of the nitroso-group and accept the implication of greater reorganisation energies at nitrogen in the liberated nitric oxide on fission of either the H–NO or $\geqslant$C–NO bonds compared with halogen–NO, –O–NO, and >N–NO.

It is of interest to explore the kinetic consequences of D(C–NO) values and in particular to relate these to the use of nitric oxide as a presumed [15] inhibitor of gaseous free radical chain reactions. Some years ago attention was drawn [16] to the fact that the removal of free radicals by nitric oxide was dependent upon the rate of reaction (1) being much larger than that of (2). Only one value is available [17] for the Arrhenius dependence of k_1 and this can be compared with $k_2/s^{-1} = 10^{15.5} \exp(-37 \text{ to } 40/RT)$ (in kcal mol^{-1}) obtained from our D(C–N) value in combination with the literature value [18] for k_{-2} and the entropies of nitrosomethane (calculated from the molecular structure parameters),[19] methyl radical,[20] and nitric oxide.[20] Combination of these values gives k_2/k_1 varying from 10^2 to 10^4 over the range 500—1000 K. Either the values for k_1 are far too low, or there are serious errors in the assumptions made. These errors could be either the assumption that reaction (1) is homogeneous, or that inhibition by nitric oxide occurs. We consider that previous warnings [15] about the complexity of presumed inhibition mechanisms are reinforced by these calculations.

$$CH_3NO \longrightarrow CH_2NOH \qquad (1)$$

$$CH_3NO \longrightarrow CH_3 + NO \qquad (2)$$

It remains for us to consider the significance of the D(C–N) value in di-t-butyl nitroxide. This can best be done by comparing it with $D(Bu^t-NH_2)$ (see Table 4) as a reference standard. The energy difference is 46 kcal mol^{-1}, and represents the reorganisation energy in the 2-methyl-2-nitrosopropane formed on C–N fission. This is entirely comparable with the calculations for D(C–N) in $H_2NO\cdot$ and $CH_3NHO\cdot$ (66 and 61 kcal mol^{-1} respectively) [21] which on comparison with $D(NH_2-H)$ (103 kcal mol^{-1}) give reorganisation energies of 37 and 42 kcal mol^{-1} on N–H fission. Another comparison is afforded by the activation energy of 10 kcal mol^{-1} for reaction (3) measured by Cowley and Sutcliffe [22] for the case of the nitroxide derived from 2,3,5,6-tetrachloronitrobenzene in tetrahydrofuran. This compared with the reference



$$Ar-N(O\cdot)(OR) \longrightarrow ArNO + \cdot OR \qquad (3)$$

---

[14] A. P. Cox, A. H. Brittain, and D. J. Finnigan, *Trans. Faraday Soc.*, 1971, **67**, 2179.

[15] B. G. Gowenlock, *Progr. Reaction Kinetics*, 1965, **3**, 171.

[16] B. G. Gowenlock, J. Trotman, and L. Batt, *Chem. Soc. Spec. Publ. No. 10*, 1957, 75.

[17] L. Batt and B. G. Gowenlock, *Trans. Faraday Soc.*, 1960, **56**, 682.

[18] N. Basco, D. G. L. James and R. D. Suart, *Internat. J. Chem. Kinetics*, 1970, **2**, 215.

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

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

[21] D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1971, **93**, 6555.

[22] D. J. Cowley and L. H. Sutcliffe, *J. Chem. Soc. (B)*, 1970, 569.

standard of $D(NH_2$–$OMe)$ (48 kcal mol^{-1})[23] gives a reorganisation energy of 38 kcal mol^{-1}. These reorganisation energies will include as the predominant term the formation of the NO π bond in the nitroso-compound and suggest that the excited S_1 state or the T_1 state of the nitroso-compound is thus some 35—50 kcal mol^{-1} above the singlet ground state level. Such an energy value corresponds to the level of the excited S_1 state in the n–π^*(N) transition. It is obvious that further detailed studies of triplet and singlet excited states of nitroso-compounds are required and that these calculations are illustrative of the order of magnitude rather than accurate in detail.

It should also be noted that our bond dissociation energy of 29 kcal mol^{-1} for di-t-butyl nitroxide is consistent with the known thermal stability of this radical, which decomposes at temperatures >125 °C [reaction (4)].

$$2Bu^t{}_2NO\cdot \longrightarrow Bu^t{}_2NOBu^t + Bu^tNO \qquad (4)$$

It seems likely[24] that this reaction does not occur *via* a direct S_H2 reaction at sp^3 hybridised carbon, but occurs *via* the dissociation mechanism (5) followed by recombination (6)

$$Bu^t{}_2NO \longrightarrow Bu^tNO + Bu^t \qquad (5)$$

$$Bu^t{}_2NO + Bu^t \longrightarrow Bu^t{}_2NOBu^t \qquad (6)$$

We thank the S.R.C. for a maintenance grant to one of us (P. J. C.) and Drs. A. P. Cox, C. K. Prout, and K. U. Ingold and Professor E. Whittle for discussion of some of the material in this paper.

[3/1057 *Received, 23rd May, 1973*]

---

[23] A. K. Hoffmann, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *J. Amer. Chem. Soc.*, 1964, **86**, 639.

[24] K. U. Ingold, personal communication.