Appearance Potential Studies of Some Geminal Substituted *C*-Nitroso-compounds

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Appearance potential measurements are presented for a series of geminal substituted nitrosoalkanes $(CH_3)_2CX{\cdot}NO$ and $D(C-NO)$ values obtained where possible.

WE have previously presented[1-3] values determined by appearance potential measurements for $D(C-N)$ in a number of *C*-nitroso-compounds. We now present mass spectral and appearance potential measurements of a range of geminal substituted nitrosoalkanes $Me_2C(X)NO$ which parallel some of our studies[4] on the photolysis of such compounds. To the best of our knowledge no mass spectral data are available for these compounds.

EXPERIMENTAL

The compounds $[Me_2C(X)NO]_{1 \text{ or } 2}$ were prepared and handled in the following manner.

$X = Br$ (*monomer*). The method of Aston[5] was employed. The compound was stored at −196 °C under high vacuum before use, subjected to repeated degassing cycles, and fractionally distilled.

$X = Cl$ (*monomer*). This was prepared by Kosinsky's method[6] and purified by preparative g.l.c. Storage and treatment in the mass spectrometer inlet system were similar to those adopted for the bromo-compound.

$X = NO_2$ (*dimer*). This was prepared and purified as in the previous studies.[4b]

$X = CN$ (*dimer*). This was prepared and purified as in previous studies.[4d]

$X = OAc$ (*dimer*). The monomer was prepared by Lown's method.[7] It was fractionally distilled twice from the reaction mixture, b.p. 38—42 °C at 12—13 mmHg, and converted into stable colourless crystals of the dimer on low temperature crystallisation from n-pentane, m.p. 7—8 °C.

$X = Ac$ (*dimer*). This was prepared by Aston and Mayberry's method[8] and the dimer recrystallised from chloroform–light petroleum.

$X = CH_2Ac$ (*dimer*). This was prepared by Harries and Jablonsky's method.[9]

$X = CO_2Me$ (*dimer*). Piloty's method[10] for the analogous ethyl compound was adapted to the corresponding methyl ester. The product was recrystallised twice from benzene–light petroleum and had m.p. 107—108 °C (decomp.) (Found: C, 45.75; H, 7.2; N, 10.85. $C_5H_9NO_3$ requires C, 45.80; H, 6.92; N, 10.68%).

The other compounds studied (2-chloro-2-methylpropane, 2,2-dichloropropane, 2-cyano-2-methylpropane) were commercial samples and were purified by repeated vacuum fractionation. Mass spectra at 70 eV and appearance potentials were measured on an A.E.I. MS 10 mass spectrometer using the techniques detailed previously.[1-3]

RESULTS AND DISCUSSION

The appearance potentials are listed in Tables 1—9. It should be noted that, although a number of the nitroso-compounds are in the dimeric form, the observed mass spectra show no peaks corresponding to fragments greater than the monomer molecular ion and that in all cases the monomer molecular ion is absent from the spectra. Such behaviour is apparently characteristic of tertiary alkyl nitroso-compounds and contrasts with primary

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and secondary alkyl nitroso-compounds [11,12] and primary aromatic nitroso-compounds.[13] Our initial objective was to obtain values for D(C–N) in these compounds so as to obtain data for comparison with other *C*-nitroso-compounds [1-3] and thus to provide additional confirmatory evidence for the possibility of an initial C–N fission in the red light photolyses of these monomers. Table 10 gives D(C–N) values based upon the appearance of NO^+ and the known value of the ionisation potential of nitric oxide. The values for X = Cl and CH_2Ac are clearly far larger than for other nitroso-compounds [1-3]

TABLE 1

Appearance potentials for Me_2CBrNO

m/e	Possible fragment ion	Appearance potential (eV)
15	CH_3^+	11.95
27	$C_2H_3^+$	14.45
29	$C_2H_5^+$	13.25
30	NO^+	11.10
31	NOH^+	12.75
39	$C_3H_3^+$	13.80
40	$C_3H_4^+$	11.80
41	$C_3H_5^+$	11.15
42	$C_3H_6^+$	11.15
43	$C_3H_7^+$	11.25
44	N_2O^+	13.15
58	$C_2H_4NO^+$	10.10
71	$C_3H_5NO^+$	10.60
72	$C_3H_6NO^+$	10.35
80	$H^{79}Br^+$	11.60
82	$H^{81}Br^+$	
121	$C_3H_6{}^{79}Br^+$	9.25
123	$C_3H_6{}^{81}Br^+$	

TABLE 2

Appearance potentials for Me_2CClNO

m/e	Possible fragment ion	Appearance potential (eV)
15	CH_3^+	13.75
27	$C_2H_5^+$	14.75
30	NO^+	12.75
35	$^{35}Cl^+$	22.70
36	$H^{35}Cl^+$	13.35
39	$C_3H_3^+$	14.35
40	$C_3H_4^+$	11.95
41	$C_3H_5^+$	11.75
42	$C_3H_6^+$	11.35
72	$C_3H_6NO^+$	11.80
77	$C_3H_6{}^{35}Cl^+$	9.70

TABLE 3

Appearance potentials for $Me_2C(NO_2)NO$

m/e	Possible fragment ion	Appearance potential (eV)
15	CH_3^+	14.20
27	$C_2H_3^+$	14.30
29	$C_2H_5^+$	13.50
30	NO^+	10.50
39	$C_3H_3^+$	14.05
40	$C_3H_4^+$	14.60
41	$C_3H_5^+$	11.40
42	$C_3H_6^+$	11.20
43	$C_3H_7^+$	11.40
58	$C_2H_4NO^+$, CNO_2^+	10.15

TABLE 4

Appearance potentials for $Me_2C(CN)NO$

m/e	Possible fragment ion	Appearance potential (eV)
15	CH_3^+	14.60
26	CN^+, $C_2H_2^+$	16.50
27	HCN^+	14.10
30	NO^+	10.20
39	$C_3H_3^+$	13.90
40	$C_3H_4^+$	12.50
41	$C_3H_5^+$	10.85
42	$C_3H_6^+$	11.35
53	$C_2H_3CN^+$	13.65
68	$C_3H_6CN^+$	9.00

TABLE 5

Appearance potentials for $Me_2C(OAc)NO$

m/e	Possible fragment ion	Appearance potential (eV)
15	CH_3^+	12.80
26	CN^+, $C_2H_2^+$	15.90
27	$C_2H_3^+$	15.30
29	$C_2H_5^+$	14.20
30	NO^+	10.80
31	NOH^+, CH_3O^+	14.20
39	$C_3H_3^+$	14.30
40	$C_3H_4^+$	12.00
41	$C_3H_5^+$	11.80
42	$C_3H_6^+$	10.70
43	$C_3H_7^+$, $C_2H_3O^+$	10.20
45	CHO_2^+, $C_2H_5O^+$	12.75
58	$C_2H_2O_2^+$, $C_2H_4NO^+$	10.30
59	$C_2H_3O_2^+$	10.35
60	$C_2H_4O_2^+$	11.35
72	$C_3H_6NO^+$	10.25
73	$C_3H_7NO^+$	10.70
101	$C_5H_9O_2^+$	9.45

TABLE 6

Appearance potentials for $Me_2C(Ac)NO$

m/e	Possible fragment ion	Appearance potential (eV)
15	CH_3^+	15.70
30	NO^+	10.50
43	$C_2H_3O^+$	11.60

TABLE 7

Appearance potentials for $Me_2C(CH_2Ac)NO$

m/e	Possible fragment ion	Appearance potential (eV)
15	CH_3^+	15.50
29	$C_2H_5^+$	14.95
30	NO^+	12.20
40	$C_3H_4^+$	15.55
41	$C_3H_5^+$	12.95
42	$C_3H_6^+$	11.30
43	$C_3H_7^+$, $C_2H_3O^+$	10.40
55	$C_3H_3O^+$	13.25
57	$C_3H_5O^+$	10.75
86	$C_4H_8NO^+$	9.40
99	$C_6H_{11}O^+$	9.65

TABLE 8

Appearance potentials for $Me_2C(CO_2Me)NO$

m/e	Possible fragment ion	Appearance potential (eV)
15	CH_3^+	14.20
30	NO^+	9.90
59	$C_2H_3O_2^+$	11.05

TABLE 9

Appearance potentials for Me_2CCl or Me_2CCN

Y	m/e	Possible fragment ion	Appearance potential (eV)
Cl	57	$C_4H_9^+$	10.86
Cl	77	$C_3H_6Cl^+$	11.38
CN	68	$C_4H_6N^+$	12.50

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and it seems probable that in these cases the ionisation process

$$e^- + Me_2CXNO \longrightarrow Me_2CX + NO^+ + 2e^-$$

results in one or both the fragments carrying excess kinetic energy. It is also possible that Stevenson's rule is contravened and that the ionisation potential of Me_2CX is lower than that for nitric oxide (9.23 eV). Consequently these two D values are upper limits only.

TABLE 10

D(C–N) values for Me_2CX–NO based upon A.P. (NO^+)

X =	Br	Cl	NO_2	CN
D (eV)	1.87	3.42	1.27	0.97
(kcal mol^{-1})	43.0	82.7	29.2	22.7
(kJ mol^{-1})	179.7	345.7	122.1	94.9
X =	OAc	Ac	CH_2Ac	CO_2Me
D (eV)	1.57	1.27	2.97	0.67
(kcal mol^{-1})	36.1	29.2	68.7	15.4
(kJ mol^{-1})	150.9	122.1	287.2	64.4

In only one case are values available for the ionisation potential of Me_2CX, namely where X = CN [14-16] the values being 9.14,[14] 8.53,[15] and 8.56 eV.[16] The former of these values implies a zero value for D(C–NO) and the latter two only 0.47 eV. It is possible that pyrolysis in the source of the mass spectrometer could occur in this case followed by subsequent ionisation to give the Me_2CCN^+ ion. A cross check on the ionisation potential of the radical can be provided by measurement of the appearance potential of Me_2CCN^+ when 2-cyano-2-methylpropane is subjected to electron impact. We obtain a value of 12.5 eV which corresponds to an ionisation potential of 9.05 ± 0.20 eV if the assumption of constancy of $D[Me_2CX–Me]$ for X = CN and Me is made.

A further method of obtaining D(C–NO) values is by a comparative method. This is useful although it may have wider error limits than the normal electron-impact technique.

We compare the appearance potentials of the same ion produced from two different compounds.

Thus,

$$\text{t-BuCl} + e^- \longrightarrow \text{t-Bu}^+ + Cl + 2e^-$$
$$\text{A.P./(t-Bu}^+) = 10.86 \text{ eV}$$
$$\text{t-BuNO} + e^- \longrightarrow \text{t-Bu}^+ + NO + 2e^-$$
$$\text{A.P./(t-Bu}^+) = 8.9 \text{ eV}^{1,2}$$

giving $D(\text{t-Bu–Cl}) - D(\text{t-Bu–NO}) = 1.96$ eV

If we take [17] D(t-Bu–Cl) = 80 kcal mol^{-1} (334.4 kJ mol^{-1}), we obtain D(t-Bu–NO) = 35 kcal mol^{-1} (146.3 kJ mol^{-1}) in good agreement with the value previously obtained.[1,2]

A similar comparison is

$$\text{t-BuCl} + e^- \longrightarrow Me_2CCl^+ + Me + 2e^-$$
$$\text{A.P.}[Me_2CCl^+] = 11.38 \text{ eV}$$
$$Me_2CClNO + e^- \longrightarrow Me_2CCl^+ + NO + 2e^-$$
$$\text{A.P.}[Me_2CCl^+] = 9.70 \text{ eV}$$

giving $D[Me_2CCl–Me] - D[Me_2CCl–NO] = 1.68$ eV

If we assume $D[Me_2CCl–CH_3]$ = 81—84 kcal mol^{-1} (*i.e.* between $[Me_3C–Me]$ and $D[Me_2CH–Me]$ [17]) then

$D[Me_2CCl–NO]$ =
42.4—45.4 kcal mol^{-1} (177.2—189.8 kJ mol^{-1})

We can also use

$$Me_2CCl_2 + e^- \longrightarrow Me_2CCl^+ + Cl + 2e^-$$
$$\text{A.P.}[Me_2CCl^+] = 11.30 \text{ eV}$$

and thus obtain

$$D[Me_2CCl–Cl] - D[Me_2CCl–NO] = 1.60 \text{ eV}$$

By comparison with D(Me–Cl) and $D(CH_2Cl–Cl)$ where Lossing's values [18] imply a drop of 8 kcal mol^{-1} we estimate $D[Me_2CCl–Cl]$ = 72 kcal mol^{-1} and thus obtain $D[Me_2CCl–NO]$ = 35 kcal mol^{-1} (334.4 kJ mol^{-1}). This is similar to the D(C–NO) values obtained for other tertiary nitrosoalkenes.[1, 2]

The bond dissociation energies $D[Me_2CX–NO]$ where X = Br, Cl, OAc, CH_2Ac, can only be determined directly if the ionisation potentials of the radicals are known and, as yet, this information is lacking. The only systematic method of estimating the ionisation potentials of radicals is based upon correlation of ionisation potentials with Taft σ^* constants but there are insufficient σ^* values to permit such correlations to be made.

It seems probable that the bond dissociation energies in all the nitroso-compounds we have studied are less than 45 kcal mol^{-1} and that on energetic grounds there is the possibility of C–NO fission by photolysis in the red region of the spectrum.

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