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Radical Reactions with Selected Organic Compounds in the Gas Phase†

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Several organic compounds for which radical reactions prior to ionization under chemical ionization (CH_4) have been discussed were subjected to gas-phase reactions with methyl and ethyl radicals. The results and their implications for proposed reaction mechanisms in a methane plasma will be discussed.

INTRODUCTION

In the CI mass spectra of various compounds (especially aromatics, heteroaromatics and organometallics) positive and negative ions of composition $[M + 14n]$ or $[M + 14n + 1]$ have been observed when hydrocarbon reagent gases are used.[2,3] Some of these ions have been identified as oxidation products ($[M - H_2 + O]$, caused by traces of O_2),[4] but attachment of hydrocarbon residues ($[M + C_nH_{2n}]$ or $[M + C_nH_{2n+1}]$) has been verified by exact mass measurements and labelling techniques in many instances. The occurrence of such species is rather disturbing as they may be confused with higher homologues present in the sample.

Relatively little is known regarding the genesis of those species. For the formation of $[M + C_nH_{2n+1}]$ generally an attack of alkyl radicals has been suggested, while for $[M + C_nH_{2n}]$ the sequences

$$M + {}^{\cdot}CH \rightarrow [M + CH]^{\cdot} \xrightarrow{+{}^{\cdot}C_{n-1}H_{2n-1}} [M + C_nH_{2n}]$$

or

$$M + {}^{\cdot}C_nH_{2n+1} \rightarrow [M + C_nH_{2n+1}]^{\cdot} \xrightarrow{+{}^{\cdot}C_nH_{2n+1}} [M + C_nH_{2n}] + C_nH_{2n+2}$$

have been formulated.[5,6] Deuterium labelling experiments demonstrate that the reagent gas is the source of the hydrocarbon moieties, but they do not give any mechanistic information. The only direct evidence has been provided by an experiment where tetracyanoquinodimethane (TCNQ) was allowed to react with the pyrolysis products of di-*t*-butylperoxide.[7] Mass spectrometric analysis of the reaction products revealed the presence of various alkylated species (mainly $[TNCQ + 2CH_3]^{+\cdot}$ and $[TCNQ + H + CH_3]^{+\cdot}$). Rate constant calculations[7] and estimates of radical concentrations in the CI plasma make it plausible that molecule/radical reactions do occur with known 'radical traps' such as TCNQ.

METHOD AND MATERIALS

In order to test the gas-phase reactions of various substrates for which addition of hydrocarbon species has been described under conditions which are comparable to those in a CI ion source a flow apparatus[8] (Fig. 1) has been constructed which allows the reaction of amounts of material sufficient for a subsequent GC/MS analysis of the reaction products. For a radical source tetramethyl lead (TML) and tetraethyl lead (TEL) have been used, the reservoir temperature of which (t_3) was adjusted (−34°C for TML, +25 °C for TEL) to maintain a vapour pressure of 93 Pa and 50 Pa, respectively. The substrate was deposited in the first heating zone the temperature of which (t_2) was adjusted to give a sublimation rate which allowed a reaction with a large excess of alkyl radicals. When not noted otherwise the pyrolysis temperature (t_1) was 550 °C which causes an immediate decomposition of the lead alkyls (Pb mirror in the first quarter of the pyrolysis zone only). Before starting the experiments the apparatus was freed from O_2 by repetitive evacuation and flushing with N_2 (during this period TML was cooled with liquid N_2, TEL with acetone/Dry Ice). The experiments were performed without a carrier gas. Reaction products of the substrates were collected at point A by cooling with a stream of air. After the end of the pyrolysis the system was allowed to cool down while being flushed with nitrogen. All substrates were tested for thermal stability under reaction conditions. The material condensed at point A was dissolved with acetone and analysed by GC/MS (Kratos MS 25 RF mass spectrometer coupled to a Carlo Erba Mega 5160 gas chromatograph, capillary column SE 52).

$Pb(CH_3)_4$ was prepared from $Pb(OCOCH_3)_4$ and CH_3MgCl as described in Ref. 9, and purified by a fractionating distillation (twice). Boiling point 110 °C (literature boiling point[10] 110 °C), purity check by GC. $\log p$ [Torr] $= 8.1596 - 1989.5/T$[K] calculated from the values given in Ref.[10]

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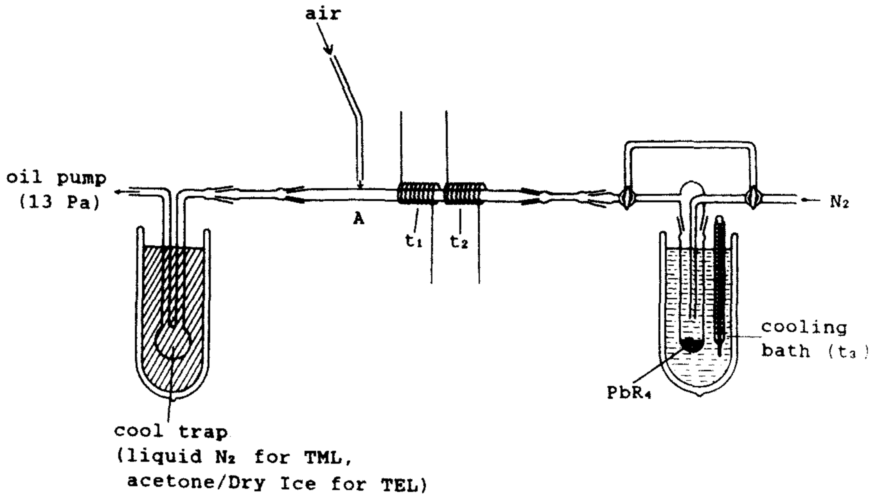


Figure 1. Flow apparatus.

$Pb(C_2H_5)_4$ commercial sample purified as above. Boiling point 75 °C/1333 Pa, purity check by GC. $\log p[\mathrm{Torr}] = 9.428 - 2938/T[\mathrm{K}]$.[11]

1,4-Di(1,1-dicyanoethyl)benzene (2)

To a mixture of 0.043 g of a suspension of NaH in mineral oil (content 60%) and 30 cm^3 freshly distilled dry tetrahydrofuran (THF) cooled to 10 °C under N_2 a solution of 0.1 g of 1,4-di(dicyanomethyl)benzene (prepared from TCNQ by reduction with HI[12]) in 20 cm^3 THF was added dropwise. After the formation of H_2 had stopped 0.14 g of freshly distilled CH_3I was added and the mixture was refluxed for 16 h. After cooling the filtered solution was evaporated to dryness and after addition of 50 cm^3 of H_2O the residue was extracted with $CHCl_3$. Usual work-up yielded 0.090 g (77%) of **2** purified by TLC and GC. Mass spectrometry: *m/z* 234 (22% relative abundance), $M^{+\cdot}$; 219 (100%), $[M - CH_3]^+$; 204 (9%), $[M - 2CH_3]^{+\cdot}$; 192 (11%), $[M - CH_3 - HCN]^+$; 165 (13%), $[M - CH_3 - 2HCN]^+$; 155 (20%), $[M - C(CH_3)_2CN]^+$. NMR ($CDCl_3$): 2.13 ppm (s, 6), $2CH_3$; 7.74 ppm (s, 4), aromatic protons.

1-(1,1-Dicyanoethyl)-4-(1-cyano-1-methyl-ethyl)benzene (1)

0.1g TCNQ and 10 cm^3 di-*t*-butylperoxide were refluxed for 3 h under N_2, then the excess of the peroxide was distilled off. The residue was dissolved in acetone and subjected to GC. The main product was **2** from which a small amount of **1** could be separated. Mass spectrometry: *m/z* 233 (11%), $M^{+\cdot}$; 208 (100%), $[M - CH_3]^+$; 129 (16%), $[M - C(CN)_2CH_3]^+$.

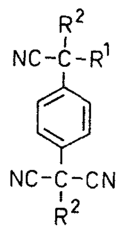
RESULTS AND DISCUSSION

TCNQ with TML

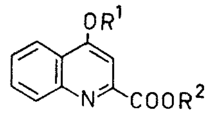
200 mg TCNQ, $t_2 = 200\,°C$, $t_2 = 200\,°C$, reaction time = 10 min, recovered material = 150 mg. The GC/MS analysis revealed two reaction products, viz. 1-(1,1-dicyanoethyl)-4-(1-cyano-1-methyl-ethyl)benzene (**1**) and 1,4-di(1,1-dicyanoethyl)benzene (**2**) in a ratio of 8:92 which could be identified by comparison with authentic material.

TCNQ with TEL

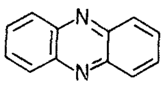
200 mg TCNQ, $t_2 = 200\,°C$, reaction time = 10 min, recovered material = 160 mg. The GC/MS analysis showed 43% starting material and 57% 1,4-di(1,1-dicyanopropyl)benzene (**3**) as could be inferred from the mass spectrum (*m/z* 262 (22%), $M^{+\cdot}$; 234 (40%),



1: $R^1 = CN$, $R^2 = CH_3$
2: $R^1 = R^2 = CH_3$
3: $R^1 = CN$, $R^2 = C_2H_5$



4: $R^1 = R^2 = H$
5: $R^1 = H$, $R^2 = CH_3$
7: $R^1 = R^2 = CH_3$



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$[M - C_2H_4]^{+\bullet}$; 207 (55%), [m/z 234 − HCN]; 205 (100%), [m/z 234 − C_2H_5].

These results are of interest for various reasons. First, the structure of **2** has been confirmed, which had before only been inferred from a corresponding ion mass in a mixture spectrum.[7] As far as CI(CH_4) results are concerned, under a variety of experimental conditions[7,13,14] ions have been observed which can be attributed only to the addition of *one* alkyl radical, even at low sample concentrations and high reagent-gas pressures, whilst in our experiments reaction of two, or even three, radicals has been observed. This confirms earlier estimates that radical additions are relatively slow in comparison with electron capture or ion–molecule reactions even with potent radical traps such as TCNQ.[7] Multiple reactions with alkyl radicals as have occasionally been suggested[6] are, therefore, rather unlikely under CI conditions. It is also of interest that ethyl radicals react apparently less readily with TCNQ than $^{\bullet}CH_3$. This makes a formation of adducts with larger hydrocarbon species in a CH_4-plasma by a primary addition of an alkyl radical rather unlikely. Whilst $^{\bullet}CH_3$ can be formed by several processes (e.g. from CH_4,[15] and also[16] from CH_5^+) and may, therefore, well exceed ionic species in abundance, higher alkyl radicals owe their existence essentially to a neutralization of alkyl ions.[7] The relative abundance[17] of $Et^+ : Pr^+ : Bu^+$ in the CH_4 plasma is roughly 1000:10:1. On the other hand, the $[TCNQ + Et]^- : [TCNQ + Pr]^-$ ratio has been found[13] as 4:1 and the intensities from $[4 + C_2H_4]^{-\bullet}$ to $[4 + C_5H_{10}]^{-\bullet}$ (see below) decrease in the ratio 10:4:2:1.[6] Unless an unexpectedly high concentration of higher alkyl radicals (note that the intensity ratios $[TCNQ + Me]^- : [TCNQ + Et]^-$ and $[4 + CH_2]^{-\bullet}$: $[4 + C_2H_4]^{-\bullet}$ are both 4:1)[6,13] is produced by a hitherto unknown mechanism the experimental data mentioned above are incompatible with substrate–alkyl radical reactions.

4-Hydroxyquinoline-2-carboxylic acid methyl ester (5) and phenazine (6) with TML and TEL

In the CI(CH_4) spectra of 4-hydroxyquinoline-2-carboxylic acid (**4**) its methyl ester (**5**) and related compounds (inter alia, phenazine, **6**) series of ions $[M + (CH_2)_n]^{-\bullet}$ and $[M + C_nH_{2n+1}]^+$ (see above) have been observed, the genesis of which has been attributed to the reaction sequence[6]

$$M + {}^{\bullet}R \longrightarrow [M + R]^{\bullet} \xrightarrow{R^{\bullet}} [M + R - H]^{\bullet} + HR$$

$$[M + R - H]^- \xleftarrow{e^-} [M + R - H]^{\bullet} \xrightarrow{H^+} [M + R]^+$$

which is in accord, inter alia, with the mass shifts observed when CD_4 was used as a reagent gas. Pyrolysis experiments were performed under the following conditions: (a) **5** with TML: 50 mg of **5**, $t_2 = 200\,°C$, reaction time = 20 min, recovered material = 40 mg; (b) **5** with TML: 50 mg of **5**, $t_2 = 190\,°C$, reaction time = 1 h, recovered material = 40 mg, (c) **5** with TEL: 50 mg of **5**, $t_2 = 190\,°C$, reaction time = 1 h, recovered material = 40 mg. In all three cases only unreacted **5** could be detected by GC or TLC; (d) **5** with TEL: 50 mg of **5**, $t_2 = 190\,°C$, reaction time = 1 h, $t_1 > 650\,°C$, recovered material = 40 mg. GC/MS analysis revealed a mixture of **5** (59%) and of 4-methoxy quinoline-2-carboxylic acid methyl ester (**7**) (41%) identified by GC, MS and TLC comparison with authentic material;[19] (e) **6** with TEL: 100 mg of **6**, $t_2 = 120\,°C$ (corresponding to a vapour pressure of 27 Pa according to $\log p\,[Torr] = 11.245 - 4705/T[K]$ calculated from the values given in Ref. 18), reaction time = 20 min, recovered material = 90 mg. In a second experiment the pyrolysis zone was filled with a fine steel wire net to increase the surface. In either case only unchanged starting material could be recovered.

The failure to observe radical reactions with **5** is in accordance with the known slow reaction of quinoline with methyl radicals in the condensed phase.[20] Phenazine has been shown to be rather reactive towards benzyl radicals[21] in the condensed phase, but nothing is known regarding its reactivity towards the less nucleophilic alkyl radicals. In any case, substrate radical reactions in the gas phase will be observed only if rate constants are appreciably higher than those for the reaction $2R^{\bullet} \rightarrow R_2$ (for $^{\bullet}Me$ and $^{\bullet}Et$, 4×10^{-11} cm^3 s^{-1}).[22] This is true for TCNQ ($k = 10^{-10}$ cm^3 s^{-1}).[7] It can be concluded that the rate constants for **5** and **6** are appreciably smaller than 10^{-11} cm^3 s^{-1}. In this case the ions $[M + (CH_2)_n]^{-\bullet}$ and $[M + C_nH_{2n+1}]^+$ observed in the CI(CH_4) spectra *cannot* be the result of a primary radical attack since ion–molecule reactions have much higher reaction constants (proton transfer and alkyl ion attachment reactions occur, e.g. with rate constants which are very close to the collision rate, i.e. $\sim 10^{-9}$ cm^3 s^{-1}).[23]

The relative nonreactivity towards $^{\bullet}Me$ and $^{\bullet}Et$ makes a primary insertion of $^{\bullet}CH$ (see above) more likely (the rate for an insertion into a C—H bond is $\sim 10^{-10}$ cm^3 s^{-1} and for O—H bonds, for example, even higher).[24] $^{\bullet}CH$ has an abundance of 1% in the mixture of primary electron ionization products[15] of CH_4 and may also be formed by secondary processes (e.g. $CH_3^+ + e^- \rightarrow CH^{\bullet} + H_2$). Also a primary reaction with CH_2 (2% amongst the primary electron ionization products of CH_4)[15] should be taken into account. In this context the observation that **5** is transformed into its 4-methyl ether under high temperature pyrolysis with TEL is of interest. The methyl ether can be formed from **5** in the condensed phase by an insertion of CH_2. CH_2, however, has not been reported as a decomposition product of TEL, at least below 600 °C. At temperatures above 600 °C $^{\bullet}Me$ rather than $^{\bullet}Et$ is formed from TEL,[25] yet the reaction $^{\bullet}C_2H_5 \rightarrow {}^{\bullet}CH_3 + CH_2$ has been reported to be favoured only if $^{\bullet}C_2H_5$ is electronically excited.[26] However, reactions such as $^{\bullet}C_2H_5 + H^{\bullet} \rightarrow CH_4 + CH_2$, and $2\,{}^{\bullet}CH_3 \rightarrow CH_4 + CH_2$ have been discussed.[27,28] Regarding a possible formation of $^{\bullet}CH$ nothing has been found in the literature.

CONCLUSION

The results reported suggest that under CI conditions, with CH_4 as a reagent gas, reactions with alkyl radicals may be expected only with known radical traps, i.e. if the reaction rate is at least 10^{-10} cm^3 s^{-1}. Multiple reactions with alkyl radicals are unlikely. There is evidence that reactions with alkyl radicals larger than $^{\cdot}$Me in a CH_4-plasma are questionable. The whole complex of alleged radical reactions prior to ionization needs apparently further experimental scrutiny.

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