# Hydride and proton transfer reactions in gaseous ion–molecule complexes [$PhCH_2^+$ $HOCH_2CH_2OH$]

**Henri E. Audier,*[a] Fadil Dahhani,[a] Arielle Milliet[a] and Dietmar Kuck*†[b]**

[a] *Département de Chimie, Laboratoire des Mécanismes Réactionnels, URA CNRS 1307, École Polytechnique, F-91128 Palaiseau, France*

[b] *Fakultät für Chemie, Universität Bielefeld, D-33501 Bielefeld, Germany and Fachbereich Chemie und Chemietechnik, Universität-GH Paderborn, D-33046 Paderborn, Germany*

**Benzyl cations and ethylene glycol react in the gas phase and form covalently bound adducts, as shown by slow and site-selective proton exchange, but also undergo irreversible hydride transfer giving two ion–neutral complexes, [$PhCH_3$ $HOCH_2CHOH^+$] and [$PhHCH_3^+$ $HOCH_2CHO$], which interconvert by a rapid and non-selective proton exchange.**

Ion–molecule reactions in the gas phase are often proceeded by hydride transfer from the neutral to the cationic partner of the encounter complex. For example, loss of methane and isobutane from protonated dimethyl ether[1] and protonated alkylbenzenes,[2–4] respectively, have been shown to occur by hydride abstraction within a complex between a cationic and a neutral fragment. In many cases, however, this process is inhibited by a variety of competing reactions; in particular, the cation may react as a proton donor (*i.e.* a Brønsted acid) rather than as a hydride acceptor (*i.e.* a Lewis acid).

A particularly interesting hydride-abstracting agent is the benzyl cation. In contrast to many alkyl cations, in particular *iso*-$C_3H_7^+$ and *tert*-$C_4H_9^+$, benzyl cations cannot react as a proton donor. Moreover, $PhCH_2^+$ is a 'soft' hydride abstractor owing to the relative weakness of the benzylic C–H bonds of toluene, and skeletal rearrangement would lead to an inert isomer, *viz.* the tropylium ion.

Here we present our preliminary results on the ion–molecule reactions between benzyl cations and ethylene glycol, a rare case in which the formation of isomeric covalent and complex-bound intermediates resulting from a hydride transfer reaction can be demonstrated. Benzyl cations were generated in the presence of ethylene glycol in the chemical ionization source of a double-focusing mass spectrometer using water as a reagent gas.‡ Adduct ions of elemental composition $C_9H_{13}O_2^+$ (charge-to-mass ratio *m/z* 153) were formed and then accelerated and separated from all other ions by a fixed, constant magnetic sector field. In general, ions thus selected have lifetimes of at least *ca.* 10–30 μs. A fraction of ions having internal energies slightly above the fragmentation threshold are 'metastable' and may decompose spontaneously within the field-free region following the magnetic sector. The fragmentation products of these metastable ions is determined by scanning the subsequent electrostatic sector field, and the MIKE spectrum[5]§ obtained provides information on the unimolecular reactions occurring during the lifetime of the (adduct) ions.

Metastable adduct ions (*m/z* 153) formed from $C_7H_7^+$ and ethylene glycol undergo essentially three competing reactions: (i) reformation of the reactants to give ions of *m/z* 91, (ii) hydride abstraction to give ions of *m/z* 61, and, as the major contribution, (iii) formation of ions of *m/z* 93, *i.e.* protonated toluene, by a formal double hydrogen transfer.[6,7]

Protonation of 2-benzyloxyethanol yields the same products with different relative contributions (given above in parentheses), an effect which is attributed to the differences in the internal energies of the adduct ions formed by the two alternative routes.[8] Water loss is only a minor process in both cases [9(2)%].

All of the three major reaction channels (i)–(iii) are subject to mass shifts if suitable deuterium labelled precursors are studied. The results of these experiments (Table 1) indicate that only the phenylic and hydroxy group hydrogen atoms undergo exchange whereas the benzylic methylene group participates neither in hydrogen exchange nor in hydrogen transfer steps (*cf.* entries 1 and 2). The metastable adduct ions $C_9H_{13}O_2^+$ form slowly interconverting covalently bound intermediates (**2** and **3**), and rapidly interconverting ion–molecule complexes (**4** and **5**), as illustrated in Scheme 1.

Only one adduct reaction (**1** → **4**) is irreversible. Introduction of methylene group labels in the glycol molecule (entry 3) leads to distinct mass shifts for channels (ii) and (iii) together with a decrease in their relative weight; at the same time, channel (i) does not undergo a mass shift but strongly gains importance. The data clearly show that the benzyl cation abstracts a hydride ion from one of the glycol methylene groups and that this is the rate-determining step of both channels (ii) and (iii). In agreement with this, labelling of the glycol hydroxy groups (entry 4) does not significantly affect the relative weights of the three channels; however, it reveals a proton exchange between the OH groups and the aromatic nucleus [*cf. m/z* 61–63 (ii), *m/z* 91–93 (i) and *m/z* 94–95 (iii)].

The existence of a rate-determining step allows us to distinguish two kinds of proton exchange processes. In particular, the formation of $C_7(H,D)_7^+$ is preceded by a slow exchange whereas the ions $C_2(H,D)_5O_2^+$ and $C_7(H,D)_9^+$ generated after hydride transfer are the subject of a relatively fast exchange. Moreover, the data from the (ring-[$^2H_3$])-labelled isotopomer (entry 5) demonstrates that the exchange preceding the re-formation of $C_7H_7^+$ involves only the hydroxy protons and those at the *ortho* positions of the benzene ring, as is evident from the exclusive formation of $C_7H_4D_3^+$ ions (*m/z* 94, instead of ions *m/z* 92–94). In contrast, the other two channels again show much more efficient H/D exchange, apparently involving all of the ring protons.¶ Finally, all the above-mentioned features, including the altered relative weights of the three reaction channels, are confirmed when perdeuteriated benzyl cations are used as precursors (entries 6 and 7); in particular, the slow $H^{OH}/H^{ortho}$ exchange occurring in channel (i) is corroborated by the formation of $C_7HD_6^+$ (*m/z* 97).

The site-specific proton exchange necessarily occurs *via* covalently bound species **2** and **3**.‖ The fact that neither the benzylic methylene nor the *meta* and *para* protons are involved

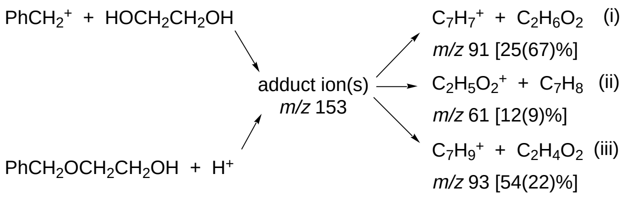
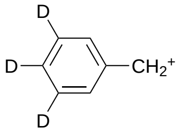
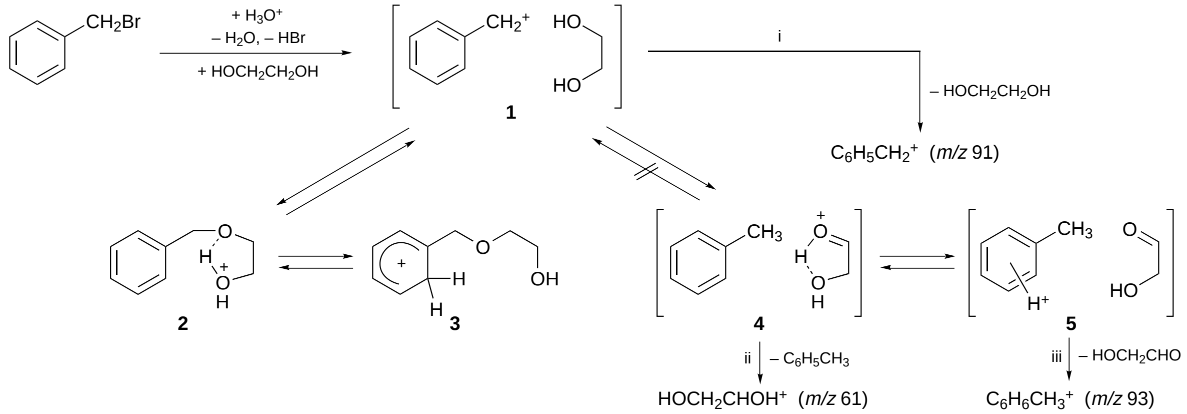


**Table 1** Partial MIKE spectroscopic data of deuterium labelled adduct ions of benzyl cations and ethylene glycol‡[a]

| | Precursors | | Product ions [glycol − H]$^+$ *m/z* | | | | | | Product ions [$C_7(H,D)_7^+$] and [$C_7(H,D)_9^+$] *m/z* | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Entry | Benzyl cation | Glycol | 61 | 62 | 63 | 64 | 65 | 66 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 | 101 |
| 1 | $PhCH_2^+$ | $HOC_2H_4OH$ | 12 | | | | | | 25 | | 54 | | | | | | | | |
| 2 | $PhCD_2^+$ | $HOC_2H_4OH$ | 12 | | | | | | — | — | 22 | — | 54 | | | | | | |
| 3 | $PhCH_2^+$ | $HOC_2D_4OH$ | — | — | — | 8 | — | | 49 | — | — | 35 | — | — | — | | | | |
| 4 | $PhCH_2^+$ | $DOC_2H_4OD$ | 3 | 5 | 4 | | | | 18 | 4 | 3 | 24 | 30 | | | | | | |
| 5 |  | $HOC_2H_4OH$ | 7 | 5 | 1 | — | | | — | — | — | 29 | 15 | 42 | | | | | |
| 6 | $C_6D_5CD_2^+$ | $HOC_2H_4OH$ | 2.5 | 3.0 | 2.5 | — | — | — | | — | — | — | — | — | 3 | 38 | 25 | 19 | |
| 7 | $C_6D_5CD_2^+$ | $HOC_2D_4OH$ | | | | 1.5 | 2.0 | 1.5 | | | | | | — | 6 | 53 | — | 15 | 11 |

[a] Relative abundances given in % Σ.



Scheme 1

clearly excludes the intermediacy of the tropylium ion.[9,10] In agreement with this, a *meta*-methyl group strongly enhances the efficiency of the proton exchange owing to an increase of the local proton affinity of the ring positions *ortho* to the side chain.[11,12]

This work has been supported by the European Commission (HUCAMO Project No. CHRX-CT93 0291, 'Fundamental Studies in Gas-phase Ion Chemistry and Mass Spectrometry') and by the Fonds der Chemischen Industrie.

## Footnotes

† E-mail: kuck@chema.uni-bielefeld.de

‡ All experiments were performed using a ZAB-2F double focusing mass spectrometer (VG Micromass, Manchester) with reversed Nier-Johnson geometry. Ions were generated by a chemical ionization source at a nominal pressure of *ca.* $10^{-5}$ mbar and at *ca.* 150 °C after introduction of the corresponding benzyl bromide (10 μl), ethylene glycol (10 μl) and water (30 μl).

§ MIKES: Mass-analysed ion kinetic energy spectrometry.

¶ The proton exchange **4** ⇌ **5** is apparently statistical if the predominant interchange of the *ortho* and *para* protons of the aromatic ring and the two oxygen-bound protons of the glycol is assumed. This result is in agreement with the almost identical proton affinities of toluene [190 kcal mol$^{-1}$ [13] (for *para* protonation) and 188 kcal mol$^{-1}$ (for *ortho* protonation[11,12]] and that of hydroxyacetaldehyde [189 kcal mol$^{-1}$ (measured recently in our laboratories)] (1 cal = 4.184 J).

‖ Hydrogen atom transfer giving the complex [6-methylenecyclohexadiene$^{\cdot+}$ $\cdot OC_2H_4OH$] can be safely discarded as it requires *ca.* 250 kJ mol$^{-1}$ starting from **1**.

## References

1 H. E. Audier, G. K. Koyanagi, T. B. McMahon and D. Thölmann, *J. Phys. Chem.*, 1996, **100**, 8220.

2 D. Berthomieu, V. Brenner, G. Ohanessian, J. P. Denhez, P. Millié and H. E. Audier, *J. Phys. Chem.*, 1995, **99**, 712; see also H. E. Audier, C. Monteiro, P. Mourgues and D. Berthomieu, *Org. Mass Spectrom.*, 1990, **25**, 245.

3 D. Kuck and C. Matthias, *J. Am. Chem. Soc.*, 1992, **114**, 1901.

4 C. Matthias, K. Weniger and D. Kuck, *Eur. Mass Spectrom.*, 1995, **1**, 445; see also D. Kuck, *Int. J. Mass Spectrom. Ion Process*, 1992, **117**, 441.

5 R. G. Cooks, J. H. Beynon, R. M. Caprioli and G. R. Lester, *Metastable Ions*, Elsevier, Amsterdam, 1973; J. R. Chapman, *Practical Organic Mass Spectrometry*, Wiley, Chichester, 2nd edn., 1993.

6 R. D. Bowen, *Acc. Chem. Res.*, 1991, **24**, 364.

7 D. Kuck and U. Filges, *Org. Mass. Spectrom.*, 1988, **23**, 643.

8 F. W. McLafferty and F. Tureček, *Interpretation of Mass Spectra*, University Science Books, Mill Valley, 4th edn., 1993, ch. 7.

9 D. Kuck, *Mass Spectrom. Rev.*, 1990, **9**, 187 and references cited therein.

10 For a recent review on the chemistry of gaseous benzyl and tropylium ions, see C. Lifshitz, *Acc. Chem. Rec.*, 1994, **27**, 138.

11 J. L. Devlin, J. F. Wolf, R. W. Taft and W. J. Hehre, *J. Am. Chem. Soc.*, 1976, **98**, 1990.

12 D. Kuck, *Mass Spectrom. Rev.*, 1990, **9**, 583 and references cited therein.

13 S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data*, 1988, **17**, Suppl. No. 1.

*Received, 21st August 1996; Revised manuscript received, 14th November 1996; Com. 6/07744G*