The Reaction of CH_4^+, CH_3^+, and Other Simple Carbocations with Benzene in the Gas Phase

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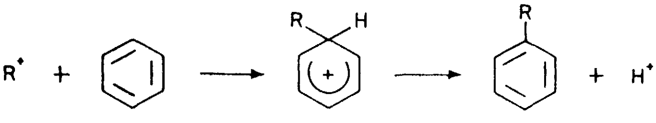
The reactions of simple carbocations with neutral benzene molecules have been studied in a triple quadrupole mass spectrometer, which has been described previously. The apparatus can be used to determine quantitatively all the cationic products of these ion-molecule reactions. Four types of reaction have been observed: (i) simple charge exchange, (ii) hydrogen atom transfer, (iii) charge exchange with hydrogen-atom scrambling, and (iv) disproportionation, also with hydrogen atom scrambling. No adduct ions of the type postulated as intermediates (' Wheland Intermediates ' or ' σ-complexes ') in Friedel–Crafts alkylation reactions in solution, were observed.

FRIEDEL–CRAFTS alkylation of benzene is usually pictured as involving the attack by a carbocation with the transient formation of an adduct cation (variously called a ' Wheland Intermediate ' or ' σ-complex ') which loses a proton to give the alkylbenzene.



SCHEME

The fate of the proton depends on the source of the carbocation R^+ and the nature of the solvent. In the majority of text-books on organic chemistry these reactions are depicted as shown in the Scheme, and although the presence of solvent is assumed (or alternatively the surface of a catalyst) no mention is usually given as to the part it must play in these reactions. The present work is an attempt to study these reactions in the gas phase completely free from a solvent (or a catalyst surface).

Ion–molecule reactions in the gas phase have been studied by high pressure mass spectroscopy,[1] two stage ion-beam mass spectroscopy,[2] ion cyclotron resonance,[3] and tandem (magnetic sector) mass spectrometry.[4] Recently also there has been a study of ' gas-phase ' reactions using cations generated by radioactive decay.[5] This is interesting work, but since the reactions occur in sealed tubes at elevated temperatures, relatively high pressures, and involve reaction times of several months the importance of three body collisions at the wall cannot be discounted. Certainly the results obtained using CT_3^+ generated by radioactive decay and the present mass spectrometric work using CH_3^+ and CD_3^+ are at complete variance.

EXPERIMENTAL

The triple quadrupole [6] consists of, in series, the first quadrupole (mass filter); the second radiofrequency-only quadrupole (collision chamber); the third quadrupole (mass filter), and an electron multiplier.

Ions formed by electron impact are mass-analysed and mass value of *m*/*z* selected by the first quadrupole. Ions emerging from this pass into the second quadrupole which holds ions with masses over a wide range of *m*/*z* in stable trajectories. The collision gas is admitted to this region, and collision reactions take place here. Differential pumping between the ion source and collision region prevents mixing of the neutral reagent gases. Ions formed in these reactions are mass-analysed by the third quadrupole, and detected by the electron multiplier.

The ionization source is of conventional Nier type using a transverse electron beam. The ionizing energy was 55 eV. Ions were drawn out of the source by an electrode at −90 V, then focused on the entrance aperture to the first quadrupole, which was at a potential of −10 V.

Operating conditions in the three quadrupoles were as given in Table 1.

TABLE 1

Operating conditions for quadrupoles

	Q_1	Q_2	Q_3
Alternating current frequency (MHz)	2.0	2.8	2.0
$V_{a.c.}$ (r.m.s.)	420	175	420
Mean translational energy along axis (eV)	8.5	0.8	10.0
Effective mass resolution	100		100

Trajectory calculations carried out using a simulation program,[7] suggested that under the above conditions, the mean spread in energies of the primary ions in the second quadrupole due to its radiofrequency field was < 1 eV.

The primary ions of type CH_4^+, CH_3^+, CH_2^+, and CH^+ have been prepared by electron impact on CH_4 (Commonwealth Industrial Gases) and CD_4. The primary ions $C_2H_5^+$ and $C_2H_3^+$ were prepared by electron impact on ethyl iodide, and $C_3H_7^+$ and $C_3H_5^+$ by electron impact on 2-iodopropane.

Benzene was AnalaR (May and Baker) and hexadeuteriobenzene was 99.5% C_6D_6 (Aldrich).

Cross sections measured with the instrument were calibrated by projecting Ar^+ ions into N_2 gas, and examining the charge-transfer process. The cross-section for this reaction is well established.[8] The ratio of the primary ion current with no reactant gas in the second quadrupole, to the secondary ion current produced with a known benzene pressure was then compared with the corresponding values for the ratio $N_2^+ : Ar^+$. The instrumental characteristics can thus be eliminated and the cross-section calculated.

The results obtained in the present work should differ from those obtained using ion beams with energies in excess of 1 kV. The reactions might be expected to take place on the same electronic potential surface. The primary energy is well characterised, unlike that of ions formed in high pressure chemical ionization sources. In contrast to the tandem magnetic sector mass spectrometer, which discriminates in favour of ions formed by simple charge exchange over ions formed in a collision,[4b] the triple quadrupole discriminates in favour of ions formed *via* an addition complex. This is because ions formed in a collision process acquire a momentum which takes them out of the extraction zone in the tandem mass spectrometer, but on into the third quadrupole in the triple quadrupole mass spectrometer. The conditions are more similar to those in an ion cyclotron resonance mass spectrometer, although it is believed that the present measurements are more dependable than those obtained using double-resonance techniques of detection.

RESULTS

CH_4^+.—The methane cation (electron recombination potential 12.70 eV) [9] reacts with benzene simply by charge exchange. The reaction is exothermic (ΔH −3.46 eV), but very little fragmentation is observed. The results of the present investigation are in good accord with those obtained in charge exchange studies according to which the electron comes from the $3e_{2g}$ electron ground state of benzene. However the studies with deuterio-labelled compounds show that some scrambling of hydrogen atoms occurred.

TABLE 2

CH_4^+ into benzene (cross section $\times 10^{17}$ cm^2)

$C_6X_6 + CY_4^+ \longrightarrow C_6X_6^+ + CY_4$

	$C_6X_6^+$	$C_6X_5Y^+$	$C_6X_4Y_2^+$	ΣQ
X = H, Y = H	6.71			6.71
X = D, Y = H	2.10	0.09	0.04	2.23
X = H, Y = D	3.20	0.04	0.06	3.30
X = D, Y = D	2.14			2.14

TABLE 3

CH_3^+ into benzene (cross section $\times 10^{17}$ cm^2)

$C_6X_6 + CY_3^+ \longrightarrow C_6X_5^+ + CY_3X$

	$C_6X_5^+$	$C_6X_4Y^+$	ΣQ
X = H, Y = H	2.87		2.87
X = D, Y = H	0.66	0.18	0.84
X = H, Y = D	2.49	0.48	2.97
X = D, Y = D	1.50		1.50

$C_6X_6 + CY_3^+ \longrightarrow C_6X_6^+ + CY_3$

	$C_6X_6^+$	$C_6X_5Y^+$	$C_6X_4Y_2^+$	ΣQ
X = H, Y = H	3.51			3.51
X = D, Y = H	1.58	0.06	0.22	1.86
X = H, Y = D	3.78	0.50	0.12	4.40
X = D, Y = D	1.90			1.90

$C_6X_6 + CY_3^+ \longrightarrow C_7X_6Y^+ + Y_2$

	$C_7X_6Y^+$	$C_7X_5Y_2^+$	$C_7X_4Y_3^+$	ΣQ
X = H, Y = H	0.67			0.67
X = D, Y = H	0.09	0.23	0.07	0.39
X = H, Y = D	0.09	0.26	0.12	0.47
X = D, Y = D	0.21			0.21

CH_3^+.—In sharp contrast to the methane cation the methyl cation (electron recombination potential 9.84 eV) [9] reacts with benzene by hydrogen transfer and disproportionation in addition to simple charge exchange [reactions (1)—(3)]. As Table 3 shows the predominant process is still charge exchange but hydrogen (hydride ion) abstraction is almost

$$CH_3^+ + C_6H_6 \longrightarrow C_6H_5^+ + CH_4 \qquad (1)$$

$$CH_3^+ + C_6H_6 \longrightarrow C_6H_6^+ + CH_3 \qquad (2)$$

$$CH_3^+ + C_6H_6 \longrightarrow C_7H_7^+ + H_2 \qquad (3)$$

as important. As with the methane cation charge exchange is to some extent accompanied by hydrogen scrambling. The disproportionation reaction to give the $C_7H_7^+$ ion and molecular hydrogen is associated with complete scrambling of the hydrogens on the carbon derived from the methyl cation.

TABLE 4

CH_2^+ into benzene (cross section $\times 10^{17}$ cm^2)

$C_6X_6 + CY_2^+ \longrightarrow C_6X_6^+ + CY_2$

	$C_6X_6^+$	$C_6X_5Y^+$	ΣQ
X = H, Y = H	3.50		3.50
X = D, Y = H	1.09	0.09	1.18
X = H, Y = D	3.89	0.37	4.26
X = D, Y = D	3.50		3.50

$C_6X_6 + CY_2^+ \longrightarrow C_7X_6Y^+ + Y$

	$C_7X_6Y^+$	$C_7X_5Y_2^+$	ΣQ
X = H, Y = H	1.09		1.09
X = D, Y = H	0.23	0.36	0.59
X = H, Y = D	0.23	0.69	0.92
X = D, Y = D	0.60		0.60

CH_2^+.—The methylene cation (electron recombination potential 10.39 eV) [9] behaves similarly to the methyl cation and both hydrogen transfer and disproportionation are observed in addition to charge exchange [reactions (4)—(6)]. The hydrogen transfer is, however, a very

$$CH_2^+ + C_6H_6 \longrightarrow CH_3 + C_6H_5^+ \qquad (4)$$

$$CH_2^+ + C_6H_6 \longrightarrow CH_2 + C_6H_6^+ \qquad (5)$$

$$CH_2^+ + C_6H_6 \longrightarrow H + C_7H_7^+ \qquad (6)$$

minor process and was only observed in the unsymmetric reactions (*i.e.* in $CH_2^+ + C_6D_6$ and $CD_2^+ + C_6H_6$ the cross sections were small, $\leqslant 0.2 \times 10^{-17}$ cm^2).

CH^+.—The CH cation (electron recombination potential 10.64 eV) [9] was more difficult to study because it is formed in much poorer yield from electron impact on methane than the other three ions. It underwent disproportionation in addition to charge exchange [reactions (7) and (8)].

TABLE 5

CH^+ into benzene (cross section $\times 10^{17}$ cm^2)

$C_6X_6 + CY^+ \longrightarrow C_6X_6^+ + CY$

	$C_6X_6^+$	$C_6X_5Y^+$	ΣQ
X = H, Y = H	3.60		3.60
X = D, Y = H	0.76	0.06	0.82
X = H, Y = D	2.57	0.16	2.73
X = D, Y = D	2.37		2.37

$C_6X_6 + CY^+ \longrightarrow C_7X_5^+ + H_2$

	$C_7X_5^+$	ΣQ
X = H, Y = H	0.38	0.38
X = D, Y = H	0.21	0.21
X = H, Y = D	0.06	0.06
X = D, Y = D	0.12	0.12

$$C_6H_6 + CH^+ \longrightarrow C_6H_6^+ + CH \qquad (7)$$

$$C_6H_6 + CH^+ \longrightarrow C_7H_5^+ + H_2 \qquad (8)$$

$C_2H_5^+$.—The ethyl cation $C_2H_5^+$ was prepared by electron impact on ethyl iodide. The only observed reaction of the ion (electron recombination potential 8.38 eV)[9] was charge exchange. No attempt was made to use $C_2D_5^+$. The occurrence of appreciable charge exchange with benzene suggests that the ion was formed in an excited state.

TABLE 6

$C_2H_5^+$ into benzene (cross section $\times 10^{17}$ cm^2)

$$C_6X_6 + C_2Y_5^+ \longrightarrow C_6X_6^+ + C_2Y_5$$

	$C_6X_6^+$	$C_6X_5Y^+$	$C_6X_4Y_2$	ΣQ
X = H, Y = H	5.24			5.24
X = D, Y = H	5.38	0.30	0.04	5.72

$C_2H_3^+$.—This ion (electron recombination potential 9.45 eV)[9] was prepared also by electron impact on ethyl iodide. An unexpected hydrogen abstraction was observed in addition to charge exchange [reactions (9) and (10)].

$$C_6H_6 + C_2H_3^+ \longrightarrow C_6H_6^+ + C_2H_3 \qquad (9)$$

$$C_6H_6 + C_2H_3^+ \longrightarrow C_6H_4^+ + C_2H_5 \qquad (10)$$

$C_3H_7^+$.—This ion was prepared by electron impact on 2-iodopropane. It was assumed that it had the structure $CH_3\overset{+}{C}HCH_3$ and hence its electron recombination potential, 8.1 eV,[9] was well below the ionisation potential of benzene. Charge exchange, with an appreciably lower cross section was the only reaction observed (*cf.* $C_2H_5^+$).

TABLE 7

$C_2H_3^+$ into benzene (cross section $\times 10^{17}$ cm^2)

$$C_6X_6 + C_2Y_3^+ \longrightarrow C_6X_6^+ + C_2Y_3$$

	$C_2X_6^+$	$C_6X_5Y^+$	$C_6X_4Y_2^+$	ΣQ
X = H, Y = H	4.77			4.77
X = D, Y = H	2.75	0.79	0.47	4.01

$$C_6X_6 + C_2Y_3^+ \longrightarrow C_6X_4^+ + C_2X_2Y_3^+$$

	$C_6X_4^+$	$C_6X_3Y^+$	$C_6X_2Y_2^+$	ΣQ
X = H, Y = H	1.43			1.43
X = D, Y = H	0.47	0.59	0.18	1.24

$C_3H_5^+$.—This ion was also prepared by electron impact on 2-iodopropane and was assumed to have the structure $[\overset{+}{C}H_2{-}CH{=}CH_2 \longleftrightarrow CH_2{=}CH{-}\overset{+}{C}H_2]$, *i.e.* the allyl cation with a recombination potential of 8.15 eV.[9] In addition to charge exchange the ion took part in an unexpected disproportionation reaction [reactions (11) and (12)].

TABLE 8

$C_3H_7^+$ into benzene (cross section $\times 10^{17}$ cm^2)

$$C_6X_6 + C_3Y_7^+ \longrightarrow C_6X_6^+ + C_3Y_7$$

	C_6X_6	C_6X_5Y	$C_6X_4Y_2$	ΣQ
X = H, Y = H	0.47			0.47
X = D, Y = H	0.38	0.09	0.09	0.56

$$C_3H_5^+ + C_6H_6 \longrightarrow C_6H_6^+ + C_3H_5 \qquad (11)$$

$$C_3H_5^+ + C_6H_6 \longrightarrow C_7H_6^+ + C_2H_5 \qquad (12)$$

DISCUSSION

The reactions we observe can be divided into two classes, simple charge-exchange which usually has the largest cross section, and reactions which probably involve a common intermediate addition-complex. Thus for methyl ions we can distinguish the two types of process (13) and (14).

Long range charge exchange

$$CH_3^+ + C_6H_6 \longrightarrow CH_3 + C_6H_6^+$$

$$Q\ ca.\ 4 \times 10^{-17}\ \text{cm}^2 \qquad (13)$$

Reactions proceeding *via* an addition complex

$$CH_3^+ + C_6H_6 \longrightarrow$$

$$[CH_3C_6H_6]^{+*} \longrightarrow \left.\begin{array}{l} \longrightarrow C_6H_6^+ + CH_3 \\ \longrightarrow C_6H_5^+ + CH_4 \\ \longrightarrow C_7H_7^+ + H_2 \end{array}\right\}$$

$$\Sigma Q\ ca.\ 3 \times 10^{-17}\ \text{cm}^2 \qquad (14)$$

The absolute cross sections are probably only accurate within a factor of two or three, but within one series, *i.e.* the reactions of one particular primary ion with one particular target molecule, the relative cross sections should be much more accurate.

TABLE 9

$C_3H_5^+$ into benzene (cross section $\times 10^{17}$ cm^2)

$$C_6X_6 + C_3Y_5^+ \longrightarrow C_6X_6^+ + C_3Y_5$$

	$C_6X_6^+$	ΣQ
X = H, Y = H	0.32	0.32
X = D, Y = H	0.29	0.29

$$C_6X_6 + C_3Y_5^+ \longrightarrow C_7X_6^+ + C_2Y_5$$

	$C_7X_6^+$	$C_7X_5Y^+$	$C_7X_4Y_2^+$	ΣQ
X = H, Y = H	0.82			0.82
X = D, Y = H	0.05	0.35	0.12	0.52

The results for CH_3^+ attributable to the 'addition complex' route are in good accord with results previously obtained using the tandem magnetic sector spectrometer, in which the three ionic products $C_6H_6^+$, $C_6H_5^+$, and $C_7H_7^+$ have been observed.[10] They are also in accord with the very limited data obtained by ion cyclotron resonance, for the reaction of methyl cations with benzene.[11,12] Finally, they show a close similarity to the results obtained by Futrell and his co-workers for the reaction of methyl cations with ethylene.[13] The charge-exchange reactions of CH_4^+ and CH_3^+ have previously been studied with the tandem magnetic sector mass spectrometer.[10]

The most significant feature of both the present work and the earlier studies is the very extensive breaking of bonds in reactions, which although exothermic overall, involve ions and neutral molecules where electron recombination potential and ionisation potential respectively differ by <1 eV. The values for the heat of formation of many of the radicals and ions formed can only be obtained indirectly and we have not therefore attempted to calculate the various heats of reaction. Some reactions which are thermodynamically favourable are not observed but it is noticeable that in the reactions involving considerable bond breaking the products include a particularly stable molecule, radical, or ion (see Table 10).

No simple addition reactions (15)—(17) are observed.

$$CH_3^+ + C_6H_6 \not\longrightarrow C_7H_9^+ \qquad (15)$$

$$CH^+ + C_6H_6 \not\longrightarrow C_7H_7^+ \qquad (16)$$

$$(CH_3)_2CH^+ + C_6H_6 \not\longrightarrow C_9H_{13}^+ \qquad (17)$$

The absence of such reactions, two of which are considered to be well established in the solution phase, can be attributed to the exothermic nature of these reactions. Further more addition would be accompanied by a loss of free energy not associated with disproportionation.

The disproportionation reactions are all associated with hydrogen atom scrambling. There is even a small amount of hydrogen atom scrambling within the charge exchange reactions. This indicates that although most of the charge exchange may involve an electron jump through space, some of the charge exchange occurs *via* the ' addition complex '. Hydrogen atom scrambling, and even carbon atom scrambling, is well established for the benzene cation and substituted benzene cations formed by electron impact.[14] Fluorine atom migration in polyfluorobenzene cations formed by charge exchange has also been observed.[4b] The structures of the cations formed by disproportionation remain uncertain although it seems likely that the $C_7H_7^+$ ions have a planar tropylium structure. The scrambling of hydrogen atoms is very extensive by both routes (*i.e.* CH_3^+ and CH_2^+).

TABLE 10

Stable species formed in disproportionation reactions

$$\begin{array}{rl}
CH_3^+ + C_6H_6 & \longrightarrow C_6H_5^+ + CH_4 \\
 & \longrightarrow C_7H_7^+ + H_2 \\
CH_2^+ + C_6H_6 & \longrightarrow C_6H_5^+ + CH_3 \\
 & \longrightarrow H + C_7H_7^+ \\
CH^+ + C_6H_6 & \longrightarrow C_7H_5^+ + H_2 \\
C_2H_3^+ + C_6H_6 & \longrightarrow C_6H_4^+ + C_2H_5 \\
C_3H_5^+ + C_6H_6 & \longrightarrow C_7H_6^+ + C_2H_5
\end{array}$$

$$\begin{array}{llll}
CH_3^+ + C_6D_6 \longrightarrow & C_7H_3D_4^+; & C_7H_2D_5^+ \text{ and} & C_7HD_6^+ \\
 & 18\% & 59\% & 23\% \\
CD_3^+ + C_6H_6 \longrightarrow & C_7H_4D_3^+; & C_7H_5D_2^+ \text{ and} & C_7H_6D^+ \\
 & 26\% & 55\% & 19\% \\
CH_2^+ + C_6D_6 \longrightarrow & C_7HD_6^+ \text{ and} & C_7H_2D_5^+ & \\
 & 39\% & 61\% & \\
CD_2^+ + C_6H_6 \longrightarrow & C_7H_6D^+ \text{ and} & C_7H_5D_2^+ & \\
 & 25\% & 75\% &
\end{array}$$

The other two C_7 ions $C_7H_6^+$ (from $C_3H_5^+$)[13] and $C_7H_5^+$ (from CH^+) are probably linear and the same applies to the $C_6H_4^+$ ion (from $C_2H_3^+$). Exotic cyclic structures such as cyclopropenium fused to benzene for $C_7H_5^+$ and positively charged benzyne for $C_6H_4^+$, can be drawn, but these rigid structures are most likely.

Although all the reactions except the charge exchange must proceed *via* an ' addition-complex ', this complex is unlikely to have much resemblance to the ' Wheland intermediate ' (or ' σ-complex ') postulated for solution phase reactions. The reactions are all very exothermic and the benzene ring is unlikely to retain a simple planar structure. The facile hydrogen atom scrambling and the ring expansion reactions all imply very flexible high energy complexes which can relax in a large number of different ways. In solution the electrophile is held in a solvent shell and the reaction will proceed with the solvent molecules rearranging in such a way as to dissipate the positive charge as much as possible. The reaction in solution will have an appreciable energy barrier due to the changes necessary in the solvation of the electrophile and the benzene molecule. In the gas phase there is virtually no energy barrier and the transient ' addition complex ' is a high energy species which loses its excess energy by fragmentation.

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REFERENCES

[1] F. W. Lampe, J. L. Franklin, and F. H. Field, *Prog. React. Kinet.*, 1961, **1**, 67.

[2] T. P. J. Izod and J. M. Tedder, *Proc. R. Soc. London, Ser. A*, 1974, **337**, 377.

[3] L. J. Andrews, J. L. Beauchamp, R. C. Dunbar, and B. D. Baldischieter, *J. Chem. Phys.*, 1966, 45, 1062; J. H. Futrell, ' Dynamic Mass Spectrometry ', ed. D. Price; Heyden and Sons, London 1971, No. 2, p. 97.

[4] (*a*) E. Lindholm, ' Ion Molecule Reactions ', ed. J. L. Franklin, Butterworths, London, 1970, vol. 2, p. 457; (*b*) J. Jalonen, J. M. Tedder, and P. H. Vidaud, *J. Chem. Soc., Faraday Trans. 1*, 1979, 2040.

[5] F. Cacace and P. Giacomello, *J. Chem. Soc., Perkin Trans. 2*, 1978, 652.

[6] R. A. Yost, C. G. Enke, D. C. McGilvery, and J. D. Morrison, *Int. J. Mass Spectrom. Ion Phys.*, 1970, **30**, 127.

[7] D. C. McGilvery and J. D. Morrison, unpublished work.

[8] J. B. Homer, R. S. Lehrle, J. C. Robb, and D. W. Thomas, *Trans. Faraday Soc.*, 1966, **62**, 619.

[9] H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data*, 1977, **6**,

[10] J. M. Tedder and P. H. Vidaud, *Chem. Phys. Lett.*, 1979, **64**, 81, and unpublished work.

[11] S. A. Benezra, M. K. Hoffman, and M. M. Bursey, *J. Am. Chem. Soc.*, 1970, **92**, 7501.

[12] J. L. Beauchamp, ' Interaction between Ions and Molecules ', ed. P. Ausloos, Plenum Press, London and New York, 1974, p. 413.

[13] A. Fiaux, D. L. Smith, and J. H. Futrell, *Int. J. Mass Spectrom. Ion Phys.*, 1977, **25**, 281.

[14] C. G. McDonald and J. Shannon, *Aust. J. Chem.*, 1962, **15**, 771; K. R. Jennings, *Z. Naturforsch*, 1967, **229**, 454; I. Horman, A. N. H. Yeo, and D. H. Williams, *J. Am. Chem. Soc.*, 1970, **92**, 2131; R. J. Dickenson and D. H. Williams, *J. Chem. Soc. B*, 1971, 249; J. H. Beynon, R. M. Caprioli, W. O. Perry, and W. E. Baitinger, *J. Am. Chem. Soc.*, 1972, **94**, 6828; G. A. Gallup, D. Steinheider, and M. L. Gross, *Int. J. Mass Spectrom. Ion Phys.*, 1976, **22**, 185; J. L. Occolwitz and G. L. White, *Aust. J. Chem.*, 1968, **21**, 997.