Gas-phase Condensation of t-Butyl Cations with Lewis Bases

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Summary t-Butyl cations, obtained in the dilute gas phase from the radiolysis of neopentane, react with H_2O, MeOH, and EtOH giving high yields of the condensation products, t-butyl alcohol, t-butyl methyl ether, and t-butyl ethyl ether respectively; the relative rates of the condensations with H_2O and MeOH, and of proton

transfer to NH_3, are very similar in gaseous neopentane at atmospheric pressure.

CONDENSATION of carbonium ions with Lewis bases, well known in solution, is difficult to study in the gas phase. In fact, even moderately exothermic processes of the general type $A^+ + B \rightarrow AB^+$ escape detection in the pressure range available in most mass spectrometers, e.g. ion cyclotron resonance (i.c.r.) instruments, owing to the dissociation of the excited product in the absence of collisional stabilization. A more fundamental limitation arises from the failure of the 'structurally blind' mass spectrometer to establish the nature of the species formed, in particular to discriminate between genuine condensation products and mere 'solvation' adducts, arising from clustering processes. A case in point is the condensation of t-butyl cations with water [reaction (1)].

$$Bu^{t+} + H_2O \longrightarrow C_4H_{11}O^+ \tag{1}$$
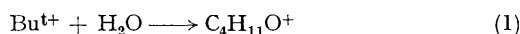
Recently Hiraoka and Kebarle,[1] confirming earlier results of Hellner and Sieck,[2] reported mass-spectrometric detection of a product characterized by the m/e ratio typical of $C_4H_{11}O^+$, and in the absence of direct evidence allowing discrimination between its possible structures, i.e. protonated t-butyl alcohol (I) or hydrated t-butyl ion (II), favoured the former, on the grounds of indirect thermochemical data. Their assignment was based mainly on the

$$\overset{+}{Bu^t{-}OH_2} \qquad\qquad Bu^{t+}{\cdot}H_2O$$
$$\quad(I) \qquad\qquad\qquad (II)$$

identity of the H_f^o of (I), calculated from the proton affinity of t-butyl alcohol, with the H_f^o of the product from reaction (1), deduced in turn from the equilibrium constant of the reaction, and can hardly be regarded as conclusive. In particular, the difference in energy between (I) and (II) is presumably small compared with the uncertainties affecting H_f^o calculations, and the complicated nature of the equilibria involved.†

In view of these considerations and the interest in reaction (1) as a general model for condensations between Lewis bases and carbocations, and evaluation of ionic contribution to prebiotic syntheses,[3] we have attempted to gather independent evidence on the structure of the product from

reaction (1) by a recent radiolytic technique capable of overcoming the lack of structural resolution of mass spectrometry, in that it allows actual isolation of the products from gas-phase ionic reactions.[4] Accordingly, the condensation (1) was investigated by irradiating (^{60}Co source; 30 °C) gaseous neopentane (100—740 Torr) containing traces of water or other nucleophiles, a radical scavenger (O_2), and a gaseous base (NH_3).

The products were identified by g.l.c., by comparison of their retention volume with that of authentic samples, or by g.l.c.–mass spectrometry. The Table gives the absolute yields of t-butyl alcohol from the neopentane–water systems, calculated from the known $G(Bu^{t+})$ values for neopentane irradiation.[5] The results show that Bu^tOH is indeed a major product, arising from the condensation (1), giving the oxonium ion (I). Since proton transfer from (I) to a single H_2O molecule is endothermic[1,6] by ca. 92 kJ mol^{-1}, deprotonation requires clustering of several water molecules according to a process represented by the overall equation (2).

$$(I) + nH_2O \longrightarrow Bu^tOH + H(H_2O)_n^+ \tag{2}$$
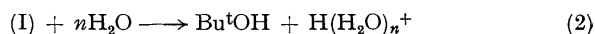
The process suffers competition from the dehydration (3) leading to isobutene, which is endothermic[1] by <17 kJ

$$(I) + nH_2O \longrightarrow iso\text{-}C_4H_8 + H(H_2O)_{n+1} \tag{3}$$
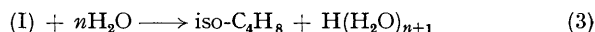
mol^{-1} when $n = 1$. This competition accounts for the fact that the yields of Bu^tOH from the irradiation of neopentane–water mixtures are lower than expected from the $G(Bu^{t+})$ value, the balance being accounted for by isobutene.

The effects of ammonia are consistent with the above scheme. In fact, on the one hand ammonia intercepts the t-butyl ions according to the exothermic[6] ($\Delta H^0 - 37$ kJ mol^{-1}) deprotonation (4), and on the other, deprotonation

$$Bu^{t+} + NH_3 \longrightarrow iso\text{-}C_4H_8 + NH_4^+ \tag{4}$$
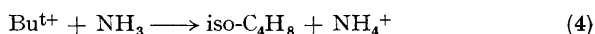
of (I) by ammonia can occur in a single-step exothermic[1,6] ($\Delta H^0 - 43$ kJ mol^{-1}) reaction, that is likely to suppress isobutene formation via the slower process (3) requiring stepwise clustering of H_2O molecules. Occurrence of
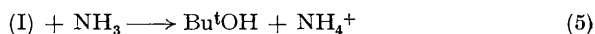
$$(I) + NH_3 \longrightarrow Bu^tOH + NH_4^+ \tag{5}$$

TABLE. Gas-phase condensation of Bu^{t+} ions with water and methanol.

Neopentane	System composition (P/Torr)				% Yields of Bu^tOH	Apparent $k(MeOH):k(H_2O)$ ratio
	O_2	H_2O	MeOH	NH_3		
720	5·0	5·3	—	3·0	64	—
720	8·0	2·7	—	20·0	9·4	—
720	9·0	12·7	—	—	41	—
720	10·0	6·9	—	—	49	—
740	6·0	5·8	8·4	3·0	—	0·7 : 1
740	5·0	2·6	17·5	3·0	—	0·7 : 1
740	2·0	13·0	3·8	2·0	—	0·9 : 1
740	8·0	17·8	2·2	4·0	—	1·0 : 1
740	8·0	3·8	2·6	3·0	—	0·7 : 1
740	10·0	12·3	2·2	4·0	—	0·9 : 1
740	8·0	3·3	0·5	—	—	1·0 : 1
740	8·0	3·9	2·8	—	—	0·7 : 1
100	10·0	3·5	2·8	3·0	—	1·1 : 1

† The difference between the stabilities of (I) and (II) cannot be larger, and is likely to be considerably smaller, than 47 kJ mol^{-1}, the full exothermicity of reaction (1). The spread of the published proton affinity values of t-butyl alcohol, necessary for calculation of the H_f^o of (I) is unfortunately of the same order of magnitude.

reactions (4) and (5) explains the effect of ammonia on the yields of Bu^tOH. At high $[NH_3] : [H_2O]$ ratios, process (4) predominates over (1) and the yields of the alcohol are substantially reduced, an observation that confirms the ionic nature of the process responsible for the Bu^tOH formation. At low $[NH_3]$, the yield of Bu^tOH reaches a maximum since reaction (1) predominates over (4), and the oxonium ions (I) formed are deprotonated *via* reaction (5), thus escaping conversion into isobutene by reaction (3). Similar sequences can be written for the formation of t-butyl methyl ether and t-butyl ethyl ether from the attack of t-butyl cations on MeOH and EtOH, which involves intermediacy of the corresponding oxonium ions $R^{-+}OH-Bu^t$.

The relative rates of proton transfer from Bu^{t+} to NH_3, and of Bu^{t+} condensation with, respectively H_2O and MeOH, are comparable in neopentane at atmospheric pressure, as shown for the latter pair by the last entries in the Table, giving an apparent $k(\text{MeOH}) : k(\text{H}_2\text{O})$ ratio in the range $0·7$—$1·1 : 1$.

The present study thus demonstrates, with the degree of certainty allowed by its isolation, the formation of a true condensation product (involving C–O bond formation) from reaction (1), and confirms the oxonium ion structure (I) for the ionic intermediate, as correctly hinted by Hiraoka and Kebarle.[1] Finally, according to general trends observed in other gaseous reactions,[7] condensation of a carbocation with a Lewis base will become the predominant process whenever proton transfer to the nucleophile is endothermic.

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[7] For the kinetic predominance of exothermic proton transfer, see ref. 4b and D. Holtz, J. L. Beauchamp, and S. D. Woodgate, *J. Amer. Chem. Soc.*, 1970, **92**, 7485.