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Temperature Effect on Gas Phase Alkylbenzene Dealkylation

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Dealkylation of ethylbenzene, propylbenzene, and isopropylbenzene by radiolytically formed $^2H_3^+$ ions has been studied in the gaseous phase as a function of the irradiation temperature. The extent of the reaction, which increases with the temperature follows the order ethylbenzene < propylbenzene < isopropylbenzene. The Arrhenius plots of empirical observed rate constants are linear over the temperature range investigated (40—100 °C) and their slopes correspond to a difference of 12.5 and 10.0 kJ mol^{-1} between the activation energies for dealkylation of ethylbenzene and isopropylbenzene, and of ethylbenzene and propylbenzene, respectively.

Gas-phase aromatic protodealkylation has been the subject of extensive investigations, carried out by mass spectrometric,[1—3] radiolytic,[4—8] and nuclear decay,[9,10] techniques. As a consequence, a vast knowledge on gas-phase chemistry of alkylbenzenium ions has developed.[11]

The radiolytic technique, analogous to that introduced by Ausloos,[12] allows the isolation of neutral end products from ion molecule reactions occurring in the gas phase. It is based[8] on the formation of a gaseous Brönsted acid, XH^+, by γ-irradiation, which, after thermalization by collision with its precursor, X, transfers a proton to a substrate, S, to form new ionic species, SH^+ whose excess of vibrational energy depends only on the difference between the proton affinities of X and S. In alkylaromatics protonation, $ArRH^+$ excited ions are formed, and their fate will depend on the excess vibrational energy and on their stability toward dealkylation, fragmentation, and isomerization reactions.[13,14]

In a study concerning the gas-phase protonation of *p*-cymene,[15] it was observed that in the competition between dealkylation and isomerization the first reaction was favored as the protonation exothermicity decreased. Such a result was ascribed to a difference of activation energies required for the two competitive processes.

Another approach to an estimation of relative empirical activation energies is that to vary the temperature of the system.

In the present work the Arrhenius plot approach is tempted in a study concerning the attack of radiolytically formed D_3^+ ($^2H_3^+$) ions on some alkylbenzenes, namely ethylbenzene and isomeric propylbenzenes, which have been selected because of their same proton affinity (799 kJ mol^{-1}).[16,17]

Experimental

Materials. Deuterium and oxygen were high-purity gases from Matheson. The aromatic hydrocarbons were gas chromatographic standards from C. Erba (Italy) and their purity, with special regard to the absence of benzene, was checked by gas chromatography at the same conditions employed for the analysis of irradiated mixtures.

Procedure. The samples were prepared as described elsewhere[10] by mixing 600 Torr (1 Torr = 133.322 Pa) of deuterium with a low pressure (generally < 1 Torr) of the selected aromatic hydrocarbon, together with oxygen (2 Torr) into 90 mL Pyrex vessels. The irradiations were carried out in a ^{60}Co Gammacell (Nuclear Canada Ltd.) at a dose rate of 4.2 kGy h^{-1} at the selected temperature. Blank experiments, performed by substituting deuterium with helium, ensured that the formation of benzene by radiolysis was negligible over the range of temperatures investigated at the reported irradiation times (7, 2, and 1 h for ethylbenzene, propylbenzene, and isopropylbenzene, respectively).

The analysis of the products was performed by gas chromatography.

Results

The yields of benzene from protonation of ethylbenzene, propylbenzene, and isopropylbenzene are plotted in Figs. 1, 2, and 3.

A clear enhancement of the amount of benzene is obtained when the temperature rises from 40 to 100 °C. It

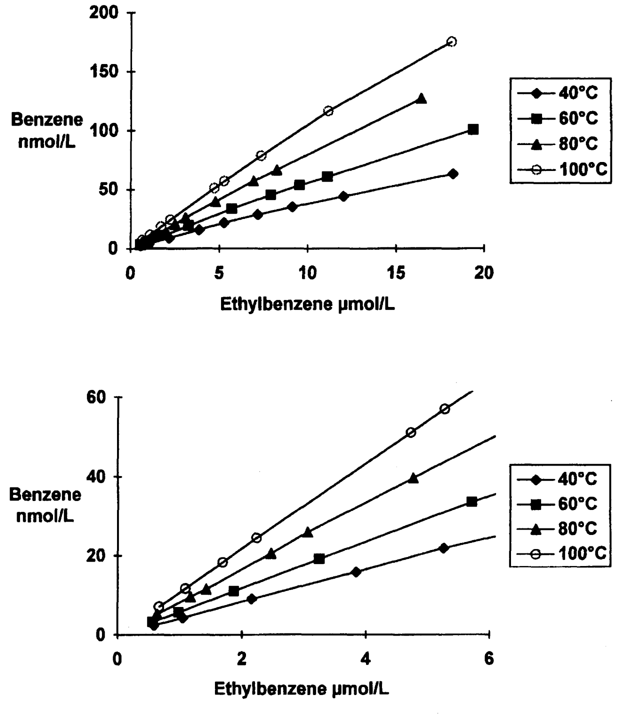

Fig. 1. Dealkylation of ethylbenzene. Irradiation time 7 h.

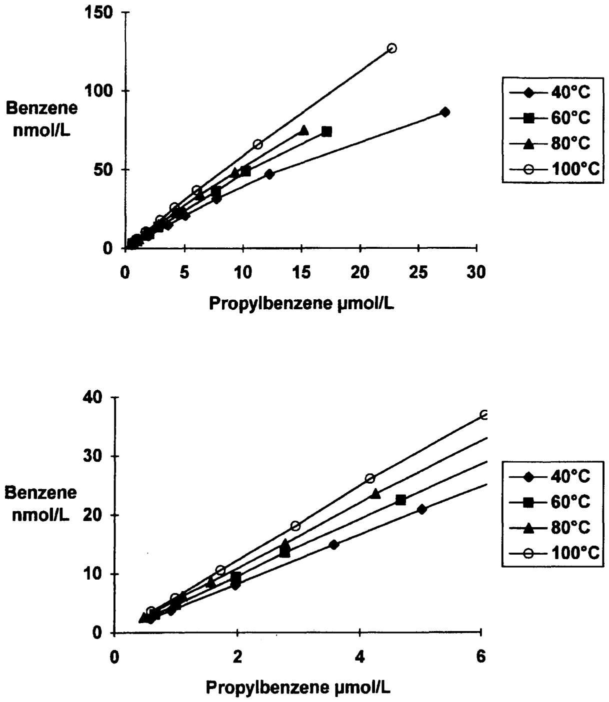

Fig. 2. Dealkylation of propylbenzene. Irradiation time: 2 h.

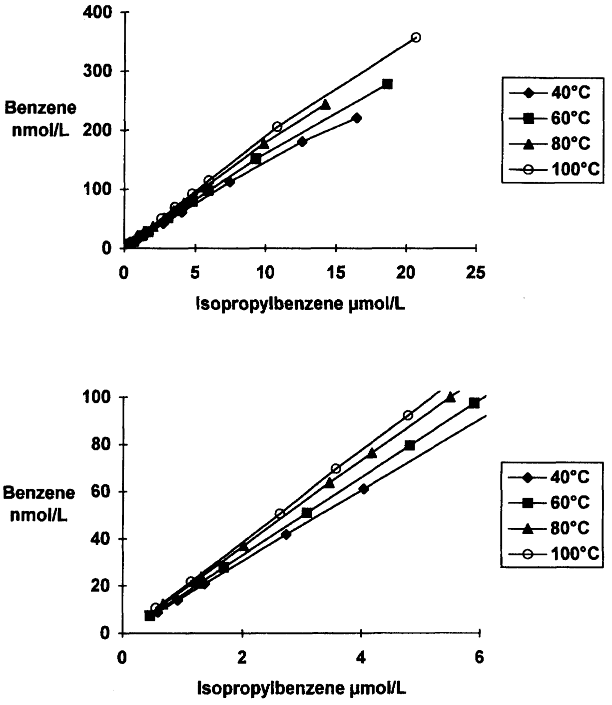

Fig. 3. Dealkylation of isopropylbenzene. Irradiation time: 1 h.

can also be observed that the yield of benzene increases in the order ethylbenzene < propylbenzene < isopropylbenzene. At the lowest substrate pressures, the yield of dealkylation product is nearly proportional to the substrate concentration.

Discussion

Since the formation of benzene by direct radiolysis of the substrate was excluded by blank experiments, and owing to the presence of oxygen an effective radical scavenger, the dealkylation reactions must be ascribed to the attack of the radiolytically formed D_3^+ ions on the aromatic hydrocarbons.

At lowest substrate pressures the yield of dealkylation is proportional to the substrate pressure within the experimental errors. In this region an observed rate constant, k_{obsd}, can be calculated from the equation:

$$[\mathrm{C_6H_6}] = k_{\mathrm{obsd}}[\mathrm{S}] \tag{1}$$

The calculated k_{obsd} values, normalized to the same adsorbed dose, are listed in Table 1.

Two reaction channels are known for the protonating ions in chemical ionization investigations: The attack on the aromatic ring to form gaseous arenium ions, which are formed with excess of vibrational energy owing to the exothermicity of the reaction[4)]

$$\mathrm{C}_n\mathrm{H}_{(2n+1)}\mathrm{Ar} + \mathrm{D_3}^+ \xrightarrow[k_\mathrm{p}]{} \mathrm{C}_n\mathrm{H}_{(2n+1)}\mathrm{ArD^+}_{\mathrm{ex}} + \mathrm{D_2} \tag{2}$$

and hydride ion abstraction from the alkyl group[1)]

$$\mathrm{C}_n\mathrm{H}_{(2n+1)}\mathrm{Ar} + \mathrm{D_3}^+ \xrightarrow[k_\mathrm{a}]{} \mathrm{C}_n\mathrm{H}_{(2n)}\mathrm{Ar}^+ + \mathrm{D_2} + \mathrm{HD} \tag{3}$$

At constant values of irradiation temperature, absorbed dose, and substrate concentration, the amount of the excited arenium ions formed will depend on the ratio between the rate constants of the two competitive reactions, favoring ring protonation in ethylbenzene.

A fraction of ions, which escapes stabilization, Eq. 4, undergoes dealkylation, Eqs. 5a and 5b with different mechanisms, as observed in chemical ionization experiments[3)]

$$\mathrm{C}_n\mathrm{H}_{(2n+1)}\mathrm{ArD^+}_{\mathrm{ex}} + \mathrm{M} \xrightarrow[k_\mathrm{m}]{} \mathrm{C}_n\mathrm{H}_{(2n+1)}\mathrm{ArD}^+ + \mathrm{M}^* \tag{4}$$

$$\mathrm{C}_n\mathrm{H}_{(2n+1)}\mathrm{ArD^+}_{\mathrm{ex}} \xrightarrow[k_\mathrm{d}]{} \begin{cases} \mathrm{olefin} + \mathrm{ArD}^+ & \text{(5a)} \\ \mathrm{C}_n\mathrm{H}_{(2n+1)}{}^+ + \mathrm{ArD} & \text{(5b)} \end{cases}$$

The stabilization occurs by collision with a moderator, M, which can be, inter alia, the substrate itself, and it is effective at substrate concentrations overwhelming 6 μmol dm^{-3} as shown in the Figs. 1, 2, and 3, while chemical ionization mass spectra[2)] established that the first mechanism (5a) is involved in ethylbenzene dealkylation, while both reaction channels are responsible

Table 1. Relative Observed Rate Constants for Dealkylation of Ethylbenzene (k_{et}), Propylbenzene ($k_{n\text{-pr}}$), and Isopropylbenzene ($k_{i\text{-pr}}$) at Different Temperatures

$T/°\mathrm{C}$	k_{et}	$k_{n\text{-pr}}$	$k_{i\text{-pr}}$
40	1.00	3.59	26.4
60	1.43	4.09	28.4
80	2.09	4.78	31.6
100	2.69	5.31	33.3

for benzene formation in propyl- and isopropylbenzene protonation.

If k_{p}, k_{a}, k_{m}, and k_{d} are the rate constants of reactions (2), (3), (4), and (5a)+(5b), respectively, a kinetic treatment will give

$$k_{\mathrm{obsd}} = \frac{k_{\mathrm{p}}k_{\mathrm{d}}[\mathrm{D_3}^+]}{k_{\mathrm{a}}k_{\mathrm{m}}[\mathrm{M}]} \tag{6}$$

Since the ratio $k_{\mathrm{p}}/k_{\mathrm{a}}$, being correlated to the number of hydrogen atoms of the aliphatic group, should increases in the order propylbenzenes<ethylbenzene, and the same proton affinity values of the alkylbenzenes[15,16] ensure that k_{m} [M] values are approximately the same for all the arenes, the differences between the observed rate constants must be ascribed to different k_{d} values.

In methylation[18] of *p*-xylene and mesitylene, and in butylation[19] of toluene and benzene by *t*-butyl ions, it was suggested that, at relatively high pressures with respect to mass spectrometric studies, the ionic intermediates formed were thermalyzed by extremely frequent collisions with the bulk component of the system, so that their internal energy approached rapidly to thermal distribution. It followed that a temperature dependence study of the observed rate constants allowed measurement of activation energy barriers, E_{o}^*, of gas phase ion molecule reactions.

Such a hypothesis seems to be in contrast with gas-phase concurrent isomerization dealkylation reactions, which were observed to be dependent on the exothermicity of protonation.[15] Negative temperature dependences of activation energies were found in mass spectrometric investigations,[20,21] where collisional deactivation is inefficient and the internal energy, E, distribution of ionic adduct may significantly differ from thermal distribution. In these conditions the measured activation energy, E^*, is dependent on the difference

$$E^* = E_{\mathrm{o}}^* - E \tag{7}$$

As shown by previous results,[15] in the protonation reactions, owing their relatively high exothermicity with respect to methylation[18] and butylation,[19] a thermal energy distribution is not reached, and the internal energy of protonated intermediate falls in the range

$$E_{\mathrm{o}} < E < \Delta H \tag{8}$$

where E_{o} and ΔH are the thermal energy of the adduct and the protonation exothermicity, respectively.

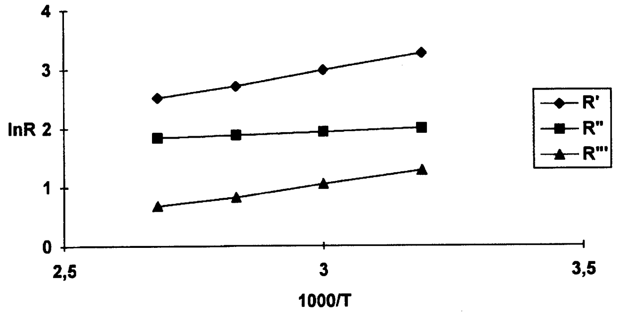

Fig. 4. Arrhenius plots. $R' = k_{i\text{-pr}}/k_{\mathrm{et}}$. $R'' = k_{i\text{-pr}}/k_{n\text{-pr}}$. $R''' = k_{n\text{-pr}}/k_{\mathrm{et}}$.

However, owing to the fact that same protonation exothermicities and identical experimental conditions ensure similar internal energy distributions for the alkylbenzenes investigated, it seems possible to obtain empirical measures of the differences between the activation energies of the investigated dealkylation processes, provided that $E < E_{\mathrm{o}}^*$.

The data, reported in Table 1, show a positive temperature dependence of observed rate constants and the Arrhenius plots of their ratios, R, give the straight lines of Fig. 4. Regression analysis of the data leads to the following differences of activation energies for dealkylation of the selected arenes:

$$E_{\mathrm{o}}^*(\mathrm{Et}) - E_{\mathrm{o}}^*(i\text{-Pr}) = 12.5\ \mathrm{kJ\,mol^{-1}} \tag{9}$$

$$E_{\mathrm{o}}^*(\mathrm{Et}) - E_{\mathrm{o}}^*(n\text{-Pr}) = 10.0\ \mathrm{kJ\,mol^{-1}} \tag{10}$$

$$E_{\mathrm{o}}^*(n\text{-Pr}) - E_{\mathrm{o}}^*(i\text{-Pr}) = 2.5\ \mathrm{kJ\,mol^{-1}} \tag{11}$$

The positive temperature dependence of the observed rate constants ensures that the internal energies of the charged adducts are lower than the activation energies required for correspondent dealkylation reactions. However, as shown by previous results,[15] the thermal energy of the adducts is not reached and, therefore, closer internal energies of the protonated intermediates allow a better approximation of the calculated activation energies differences. It might be obtained when the protonation exothermicity is the same for the substrates investigated.

Furthermore, in order to avoid annoying reactions as proton transfers from charged intermediate to neutral substrate molecules, and transalkylation reactions, which might occur when propylbenzene are protonated, the rate constants must be measured at low substrate concentrations.

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