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PREDOMINANT ORTHO ORIENTATION IN THE GAS-PHASE ISOPROPYLATION OF CHLOROBENZENE.

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Aromatic alkylation by _tert_-butyl [1,2] and _iso_-propyl [3] cations has been recently studied in the gas phase, in order to ascertain the influence of the specific ion-substrate interactions on the reactivity and the selectivity of electrophilic aromatic substitutions in the absence of solvation, ion pairing and similar effects that complicate the interpretation of solution results. This preliminary report describes the evidence for the predominant ortho isopropylation of aromatic substrates containing n-donor substituents, which appears particularly significant in the case of chlorobenzene. The alkylating reagent, _i.e_. the _iso_-$C_3H_7^+$ ion, was generated in the diluted gas phase, according to a technique previously described, based on the γ-radiolysis [1,4] of a system containing C_3H_8 as the bulk constituent, whith much smaller amounts of the aromatic substrates, in the presence of O_2 as a radicals scavenger, and when required, of a gaseous base, NH_3 or $N(CH_3)_3$. The samples, enclosed in sealed pyrex bulbs, were irradiated at 23°C to a constant dose of 2.9 Mrad, delivered at a rate of 0.46 Mrad hour^{-1}, in a ^{60}Co 220-Gammacell from Nuclear Canada Ltd, and their composition was then analyzed by glc. The results obtained at a 720 torr C_3H_8 pressure, in the presence of 10 torr O_2, are reported in the Table and refer to the isopropylation of chlorobenzene alone or in competition with toluene. These data refer exclusively to the alkylation channel, neglecting the proven protonating ability of the _iso_-$C_3H_7^+$ reagent, well documented on thermochemical and mass-spectrometric grounds. As expected for a voracious and rather unselective electrophile, such as _iso_-$C_3H_7^+$, chlorobenzene is alkylated in the gas phase at a rate comparable, if lower (about 1:2) with that of toluene, independently of the presence of gaseous bases, which however depress total yields, indicating in the first place that the deprotonation step does not influence, in the present conditions, the overall alkylation rate and, more significantly, that substitution is due to a cationic reagent. The isomeric composition of cymenes from C_7H_8 is consistent, within experimental errors, with that measured, under the same conditions, in benzene/toluene competitions, which gave a $k_{toluene}$: :$k_{benzene}$ ratio of 0.80. [3,4] In the case of both cymenes and chlorocumenes, a relatively high meta/para ratio is observed, suggesting that some isomerization cannot be excluded, even at the highest C_3H_8 pressures investigated. The isomerization process is probably intramolecular, as transalkylation reactions appear unlikely, owing to the observed constancy of the reactivity

Table.

System composition (torr)			$\frac{k_{PhCl}}{k_{PhCH_3}}$	Isomeric composition of products (%)[a]					
				Chlorocumenes			Cymenes		
PhCl	$PhCH_3$	NH_3		o-	m-	p-	o-	m-	p-
1.0				89.6	5.7	4.7			
1.8	1.2		0.54	85.0	7.2	7.8	54.8	28.2	17.0
1.4	1.4		0.56	85.8	7.0	7.2	53.4	28.9	17.7
2.2	0.4		0.46	80.9	9.8	9.3	48.4	29.3	22.2
1.0	1.0	5	0.53	78.8	10.5	10.7	45.6	29.8	24.6
1.2	1.1	5[b]	0.43	86.1	7.0	6.9	46.5	28.7	24.8

[a] Standard deviation of data ca. 5%. [b] $N(CH_3)_3$ instead of NH_3.

ratio measured at different substrates concentrations. A striking result of these experiments is the exceptionally high ortho/para ratio observed for chlorocumenes, suggesting that directing factors other than those considered in the conventional Friedel-Crafts alkylations occurring in solution are operative, whenever free and unsolvated carbonium ions are allowed to react in the gas phase with aromatic compounds bearing n-electrons donor substituents. In this connection, it is interesting to note that a "coordination effect" in the isopropylation of chlorobenzene and anisole has been suggested [5] to occur in solution, which accounts for the comparatively high ortho/para ratios observed in various electrophilic substitutions, where, however, besides the uncertainity associated with the nature of the electrophile, the influence of the counterion and of competitive solvation processes tend to obscure the specific electrophile-substrate interactions, preventing the observation of such strong bias in favour of *ortho* alkylation. In the gas phase, on the other hand, predominant attack of *tert*-$C_4H_9^+$ ions to the n-center of phenol, [2] has been previously reported, supporting the view that the present results fit into a general kinetic picture involving a competition between the two nucleophilic centers of these aromatic substrates, *i.e.* the n-center (the Cl or O atoms) and the π-center, for the gaseous carbocations, followed by subsequent collapse of the primary adduct to the ortho alkylated product.

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