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Isopropylation of Halobenzenes by *sec*-$C_3H_7^+$ Cations. Evidence for a Participation of the Substituent in a Gas-Phase Alkylation

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Abstract: Isopropylation of the halobenzenes (PhF, PhCl, and PhBr) by isopropyl cations, generated in the diluted gaseous phase from the radiolysis of propane, leads to formation of the corresponding halocumenes. The regioselectivity of the substitution changes from apparent kinetic control, i.e., ortho >80% at 760 Torr, to thermodynamic control i.e., meta, as the overall pressure is lowered to 20 Torr. The results of competitive alkylation experiments with toluene show the reactivity trend PhF > PhCl ≃ PhBr. Appreciable yields of anisole, increasing in the order PhF > PhCl ≃ PhBr, are measured when the system is radiolyzed in the presence of CH_3OH. The formation of $PhOCH_3$ is traced to the attack of methanol on the aromatic ring, activated toward nucleophilic displacement by a specific interaction of *sec*-$C_3H_7^+$ ions with the halogenated substrates. The same interaction helps also to explain the exceptionally high reactivity of the ring positions ortho to a n-donor substituent.

Introduction

Coordination effects[1,2] have long been postulated to account for high ortho/para ratios in the liquid-phase alkylation of aromatic compounds bearing n-donor substituents, such as anisole and chlorobenzene.[3] Recent studies by our group on gas-phase electrophilic aromatic substitution led to isolation of *tert*-butyl phenyl ether as the main product from the alkylation of phenol by unsolvated *tert*-butyl cations, providing direct evidence for predominant attack to the OH group, under conditions favoring kinetic control.[4] Accordingly, in the case of anisole,[5] where no neutral end product can directly arise from *tert*-butylmethylphenyloxonium ions, substantial amounts of *o*-*tert*-butylanisole have been recovered, confirming preferential reactivity of the charged electrophile toward the n-donor substituent. Analogous conclusions have been reached in the isopropylation of the same substrates by gaseous *sec*-$C_3H_7^+$ cations,[6] which can undergo either proton transfer and condensation with both "n" and "π" nucleophilic sites of phenol and anisole.

The present work has been undertaken to collect further evidence on the specific interactions of carbenium ions and n-donor substituents in the gas-phase electrophilic aromatic substitution, particularly in cases where proton transfer to the substituent is expected to be endothermic.

For this purpose, the alkylation of the halobenzenes (PhX, X = F, Cl, Br) by isopropyl cations from the radiolysis of propane has been studied in the diluted gaseous phase, where the absence of the counterion and of appreciable solvation effects brings into sharper focus the correlation between ion–molecule interactions and the formation of final neutral products.

According to a well-established technique, introduced by Ausloos and co-workers,[7] high yields of *sec*-propyl ions can be obtained from the gas-phase radiolysis of propane. This method has already been exploited,[6,8] in combination with suitable analytical techniques, to study gas-phase electrophilic aromatic substitution by *sec*-$C_3H_7^+$ ions, and consists in carrying out the radiolysis of a system, prepared by mixing trace concentrations of the substrate(s) and of appropriate additives with a large excess of C_3H_8 and a few torr of oxygen, to cut off the radical component of the process.

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Table I. Isomeric Composition of Products from the Gas-Phase Isopropylation of Fluorobenzene–Toluene Mixtures

system composition, Torr					$k_{\mathrm{PhF}}/k_{\mathrm{PhCH_3}}$	isomeric composition of products, %					
						fluorocumenes			cymenes		
C_3H_8	O_2	NH_3	PhF	$PhCH_3$		ortho	meta	para	ortho	meta	para
720	10		0.86	0.97	1.8	86	5	9	56	27	17
720	10	5	0.82	0.86	1.4	80	7	13	46	27	27
400	5		0.68	0.68	2.2	84	6	10	55	29	16
250	4		1.11	1.00	2.0	79	8	13	53	32	15
100	4		0.83	0.97	2.5	68	18	14	51	49	
20	2		0.68	0.80	4.0	44	44	12	30	70	

Table II. Isomeric Composition of Products from the Gas-Phase Isopropylation of Chlorobenzene and Chlorobenzene–Toluene Mixtures

system composition, Torr						$k_{\mathrm{PhCl}}/k_{\mathrm{PhCH_3}}$	isomeric composition of products, %					
							chlorocumenes			cymenes		
C_3H_8	O_2	NH_3	C_3H_7Cl	PhCl	$PhCH_3$		ortho	meta	para	ortho	meta	para
720	10			1.0			89	6	5			
720	10			1.8	1.2	0.54	85	7	8	55	28	17
720	10			1.4	1.4	0.56	86	7	7	53	29	18
720	10			2.2	0.4	0.46	81	10	9	48	29	22
720	10			0.5	2.9	0.54	78	12	10	50	29	21
720	10		6.8	1.0	0.8	0.28	77	12	11	51	25	24
720	10		21.5	1.2	1.3	0.18	79	11	10	53	28	19
720	10	5		1.0	1.0	0.53	79	11	10	46	30	24
500	7			0.8	0.6	0.56	77	12	11	46	32	22
400	5			1.1	0.7	0.63	78	13	9	48	33	19
400	5	3		1.1	1.0	0.52	70	15	15	40	33	27
250	5			0.7	0.5	0.64	70	17	13	45	34	21
100	4			2.5			58	30	12			
100	4			2.3	0.5	0.94	52	30	18	48	35	17
100	4			0.8	0.6	1.10	48	33	19	41	42	17
20	2			0.4	0.4	2.34	29	51	19	33	60	7

The same considerations discussed in previous papers,[6,8,9] concerning the composition of the system which minimizes direct radiolysis of the substrate(s) and favors collisional thermalization of the reagent, apply to the present study as well, which traces the formation of the alkylated products essentially to the reactions of isopropyl cations.

Experimental Section

Materials. Propane, a research grade product from Matheson Co., with 99.99% stated purity, was passed through cooled molecular sieve traps for further pruification. Research grade oxygen (Caracciolossigeno Co.) and anhydrous ammonia (Matheson Co.) with a stated purity of 99.98% were used without further purification. The halobenzenes from Fluka A.G. were purified by preparative GLC to a purity exceeding 99.99%, as determined on the same columns employed for the analysis of products. Anisole, methanol, isopropyl chloride from Merck A. G., toluene ("GC Standard") from Carlo Erba S.p.A., and trimethylamine and dimethyl ether from Fluka A.G. were commercial samples, used without further purification. Isomeric cymenes[8] and fluoro-,[10] chloro-, and bromocumenes[11] were prepared according to established procedures and purified by preparative GLC. Their identity was confirmed by mass spectrometry and by IR and NMR spectroscopy.

Procedure. The experimental techniques used for the preparation of the samples and their irradiation have been described previously.[9] The radiation dose, as measured with a Fricke dosimeter, was 2.9 Mrad, delivered at a rate of 0.55 Mrad h^{-1} at 28 °C, in a ^{60}Co Gammacell (Atomic Energy Canada Ltd.).

Control experiments at higher doses showed that the *relative* yields of products and their isomeric composition are largely independent of the dose, at least up to ca. 25 Mrad.

The analysis of the products was performed by injecting measured aliquots of the reaction mixture into a Hewlett-Packard Model 5700 A or a Perkin-Elmer Sigma 1 gas chromatograph, equipped with FID units.

The products were identified by comparing their retention volumes on at least two different columns with those of authentic samples.

Appropriate calibration curves for the detector response were determined to measure the yields of each compound.

The identity of the products was further confirmed by GC–MS, using a Hewlett-Packard Model 5982 A mass spectrometer. The same instrument, operated in the chemical ionization (CI) mode, was employed for the CI experiments. The reagent gas pressure in the source was directly measured using a Bourdon gage, inserted in place of the direct introduction probe.

The following columns were used for products analysis: (A) 8 m × 1/8 in. o.d., 10% Apiezon L grease (GAL) on Chromosorb W (acid washed), operated from 140 to 160 °C; (B) 4 m × 1/8 in. o.d., 5% polypropylene glycol on Chromosorb W (acid-washed DMCS), at 100 °C; (C) 3 m × 1/8 in. o.d., Porapak Q, at 80 and 110 °C; (D) 300 ft × 0.010 in., GAL, WCOT capillary, at 100 °C; (E) 450 ft × 0.010 in., squalane, WCOT capillary, at 40 °C; (F) 150 ft × 0.010 in. Carbowax 20M + 150 ft × 0.010 in. OV 17 capillary, from 90 to 130 °C.

The separation of the isomeric fluorocumenes was achieved on the last column.

Results

Radiolysis. The irradiation of gaseous propane in the presence of the halobenzenes or halobenzene/toluene mixtures and O_2 yields the corresponding isopropylated products, i.e., halocumenes and cymenes. Their isomeric composition, under various experimental conditions, is reported in Tables I–III, along with the system composition and the apparent substrate reactivity, as measured in competitive experiments.

The data represent the mean of at least three runs and are affected by a standard deviation of ca. 10%.

The pressure dependence of the isomeric composition of the halocumenes is plotted in Figure 1.

Moreover, the presence of methanol in the irradiation mixtures leads, in addition to alkylation, to formation of anisole from the halobenzenes but not from toluene, as shown in Table IV. No detectable amounts of isopropyl halides could be found among the neutral products from these experiments.

Control runs, carried out by irradiating systems of comparable composition but for the presence of isopropyl chloride, deliberately added in trace amounts, have shown within ex-

Table III. Isomeric Composition of Products from the Gas-Phase Isopropylation of Bromobenzene and Bromobenzene-Toluene Mixtures

system composition, Torr					k_{PhBr}/k_{PhCH_3}	isomeric composition of products, %					
						bromocumenes			cymenes		
C_3H_8	O_2	NH_3	PhBr	$PhCH_3$		ortho	meta	para	ortho	meta	para
720	10		1.2			79	9	12			
720	10		1.1	0.9	0.55	82	8	9	55	26	19
720	10		1.1	0.8	0.51	78	9	13	55	26	19
720	10		2.5	0.5	0.76	75	12	13	62	19	19
720	10		0.5	2.3	0.67	68	10	22	54	28	18
720	10	5	1.2	1.1	0.46	72	13	15	46	26	28
720	10	5[a]	1.2	0.8	0.51	74	12	14	45	29	26
400	5		1.0	0.8	0.69	76	12	12	52	29	19
250	5		1.4	1.1	0.68	60	21	19	55	28	17
100	4		1.3	1.1	0.99	39	37	24	49	36	15
20	2		0.7			31	62	7			
20	2		0.9	0.8	2.14	22	64	14	29	46	25
20	2		0.8	0.7	2.17	18	65	17	31	51	18

[a] $N(CH_3)_3$ instead of NH_3.

Table IV. Anisole Formation from the Aromatic Nucleophilic Substitution by CH_3OH on the Halobenzenes

system composition,[a] Torr				products yields %								
							isomeric composition					
							halocumenes			cymenes		
X	PhX	$PhCH_3$	CH_3OH	anisole	halocumenes	cymenes	o-	m-	p-	o-	m-	p-
		0.7	6.8			100				44	27	29
F	0.6		3.5	32	68		82	6	12			
	0.83	0.78	6.7	17	50	33	80	6	14	44	26	30
Cl	2.6		4.2	7	93		72	13	15			
	1.5		5.0	8	92		69	13	18			
	1.2		5.3	12	88		71	13	16			
	1.1		10.7	20	80		70	13	17			
Br	0.9		5.1	13	87		84	7	9			
	1.0	1.1	8.2	5	32	63	80	9	11	39	31	30

[a] $P_{C_3H_8}$ = 720 Torr and P_{O_2} = 10 Torr in all experiments.

perimental errors that any alkyl halide formed should survive to the applied radiation dose.

As previously pointed out,[6] the *absolute yields* are of rather scarce significance in experiments of this kind, since they are strongly dependent on the pressure and the composition of the system, e.g., on the presence of added base(s) or other nucleophiles in the bulk reagent gas, etc., and on the concentration of those products from the radiolysis which compete with the substrate(s) for the *sec*$C_3H_7^+$ cations.

At any rate, typical G values for isopropylated products formation, measured at 720 Torr propane, 1.0 Torr chlorobenzene, at a dose of 2.9 Mrad and in the absence of added base, amount to ca. 1.0, corresponding to an absolute yield ca. 30%, as referred to the *sec*-$C_3H_7^+$ ions produced.[7]

A sharp decrease in the G values is observed when ammonia is added to the system (with a 5 Torr NH_3 partial pressure the G value of isopropylchlorobenzenes is depressed by a factor of 10), confirming the ionic nature of the alkylation processes, as NH_3 is well-known to efficiently deprotonate *sec*-$C_3H_7^+$ ions to propene.

Chemical Ionization. To gather direct experimental evidence on the ionic intermediates involved in the alkylation process, the C_3H_8 CI spectra of the halobenzenes were recorded in the pressure range from 0.1 to 1.6 Torr at a source temperature of 168 °C, by introducing, through a heated inlet, a propane + 0.1 mol % PhX gaseous mixture into the mass spectrometer.

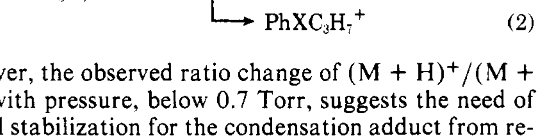
While a detailed mass spectrometric study of the system is beyond the scope of the present work, the following experimental observations will be useful in the discussion.

The $(M + H)^+/(M + C_3H_7)^+$ ion-abundance ratio decreases with increasing the source pressure, leveling off to a value depending on the nature of the aromatic substrate, for pressures higher than 0.7 Torr.

The experimental values for the protonation/condensation ratio are 1.5 for PhF, 1.7 for PhCl, and 2.3 for PhBr, as measured using systems whose composition was comparable with that employed in the radiolytic experiments. Under the same experimental conditions, toluene yields a $(M + H)^+/(M + C_3H_7)^+$ ratio in excess of 3.0, consistently with the higher proton affinity of $PhCH_3$ with respect to the halobenzenes.

Discussion

The ion abundances from CI spectra indicate that thermalized isopropyl cations, the major ions in propane plasma, react with the halobenzenes essentially via two channels, i.e., proton transfer (1) and condensation (2).



Moreover, the observed ratio change of $(M + H)^+/(M + C_3H_7)^+$ with pressure, below 0.7 Torr, suggests the need of collisional stabilization for the condensation adduct from reaction 2 to survive.

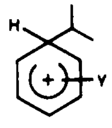
This is in agreement with the expectation, since collisional stabilization effects have been observed by Bone and Futrell[12] for the reaction of $C_3H_7^+$ ions with benzene, at pressures up to 25 μ, and the associated energetics is comparable with that pertinent to the attack on the halobenzenes.

Energetics of the *sec*-$C_3H_7^+$ Ions Attack. Using an $H_f°$ value of 190 kcal mol^{-1} for *sec*-$C_3H_7^+$,[13] the formation enthalpies of neutrals from ref 14, and the proton affinities

(PA) reported by Kebarle and co-workers for the halobenzenes,[15] reaction 1 should be exothermic by 1.2–1.6 kcal mol^{-1} for all substrates. These estimates are very likely referred to the most stable of the possible ring-protonated isomers, e.g., those protonated at a position para to the substituent.

It is interesting to point out in this connection that proton transfer from isopropyl cations to the halogen atom of the substrates is expected to be endothermic, as propene has a higher PA than the methyl halides.[16] Protonation of the latter occurs at the halogen atom,[16b] whose PA is expectedly higher than those of phenyl-substituted halogen atoms. In the case of toluene, reaction 1 is exothermic by ca. 9 kcal mol^{-1}.

For the condensation reaction 2, which represents the primary aim of the present study and leads to formation of isolable end products, a precise evaluation of the $\Delta H°$ values associated with the halobenzenes is prevented by the lack of the pertinent thermochemical data. In fact, it would be necessary, inter alia, to know the heats of formation for haloarenium ions like I, bearing the proton and the alkyl group at the same ring position.



(Y= CH_3, F, Cl, Br)

I

Nevertheless, a tentative estimate of the $\Delta H°$ for reaction 2 can be arrived at by assuming that the PA at the ring position bearing the isopropyl group is very close to that of the corresponding halobenzene,[17] and calculating the $H_f°$ of the halocumenes by group additivity rules.[18]

Accordingly, the reaction enthalpies for the alkylation process (2) at the ring position para to the substituent are expected to be ca. −27 kcal mol^{-1} for PhF, PhCl, and PhBr and −35 kcal mol^{-1} for $PhCH_3$.

The trend of the protonation/condensation ratio with pressure is consistent with this thermochemical picture, indicating the need of greater collisional stabilization to ensure survival of the $(M + C_3H_7)^+$ condensation adduct, in comparison with the $(M + H)^+$ ion.

Reactivity and Selectivity of Radiolytically Formed sec-$C_3H_7^+$ Cations. Once it is experimentally established that *sec*-$C_3H_7^+$ ions can both condense with and transfer a proton to the aromatic substrates, the formation of ions corresponding to mass $(M + H)^+$ and $(M + C_3H_7)^+$ can be assumed to occur in the radiolytic experiments as well. Of course, only the alkylation channel is directly evidenced by isolating the neutral end products from radiolysis runs, while concomitant formation of the protonated substrates can merely be postulated to take place, as thermochemically allowed and by analogy with CI observations.

Direct extrapolation of the CI data to the pressure range typical of radiolytic experiments is difficult, in view of the possible contribution, at elevated pressures, from higher order processes, and the protonation/condensation ratio from CI measurements must therefore be regarded only as a limit for high-density systems. Nevertheless, the appreciable differences found among toluene and the halobenzenes, reflecting different substrate basicities, are likely to extend to higher pressure as well, and to influence the alkylation yields from the halobenzenes as compared to toluene. In the remaining part of the discussion we will attempt to outline a unified mechanistic picture that accounts for experimental observations in the whole pressure range and provides a correlation between mass spectrometric and radiolytic results.

The yields of isopropylated products from the radiolysis can be traced to a straightforward reactions sequence, involving primary attack of the charged electrophile on the substrate(s), leading to formation of haloarenium ions I, which eventually undergo deprotonation by any base contained in the system, including the substrate itself (eq 3).

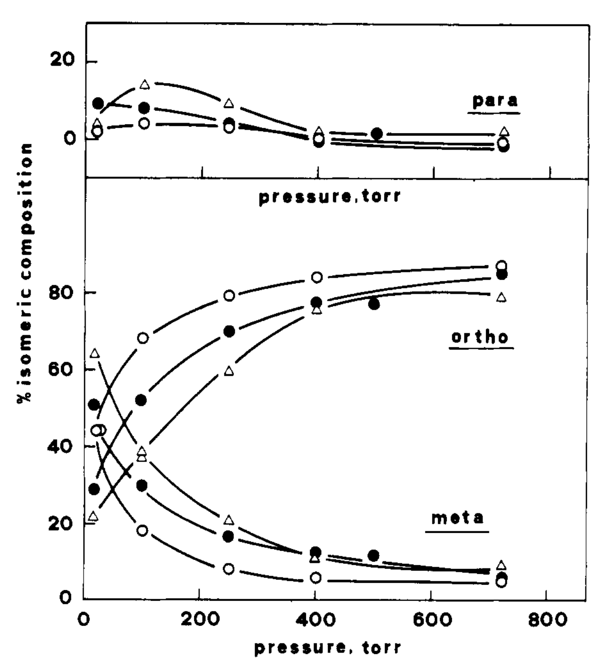
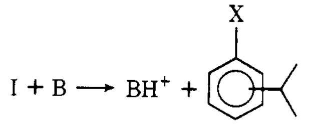


Figure 1. Pressure dependence of the isomeric composition of the halocumenes from the gas-phase alkylation of the halobenzenes by *sec*-$C_3H_7^+$ cations: fluorocumenes (○), chlorocumenes (●), bromocumenes (△).



(3)

The reactivity of *sec*-$C_3H_7^+$ ions toward the halobenzenes, as apparent from the data of Tables I–III, follows the trend PhF > PhCl $\simeq$ PhBr. Fluorobenzene undergoes alkylation more efficiently than toluene, while the $k_{PhX}:k_{PhCH_3}$ ratio for the other halobenzenes, at 720 Torr, is ca. 0.5, as calculated assuming a first-order dependence of the rates in the aromatics.

Addition of a strong base (NH_3 or $N(CH_3)_3$), while depressing the absolute yields of products, does not appreciably affect the relative alkylation rates, indicating that the eventual deprotonation step (3) is not rate determining. Furthermore, the $k_{PhX}:k_{PhCH_3}$ ratios do not significantly depend on the relative concentration of the substrates, suggesting that transalkylation processes do not appreciably contribute, at high pressure, to product formation.

Under such experimental conditions, high efficiency of collisional deactivation and the presence of a strong base are expected to favor kinetic distribution of products, which corresponds to very high ortho substitution. In fact, as shown in Tables I–III, the relative yields of ortho halocumenes appear exceptionally high if compared with the corresponding isomeric composition of cymenes and represent the most striking feature of the gas-phase electrophilic aromatic substitution.

As it cannot be accounted for simply invoking substituent electronic effects on the ring, this observation provides strong evidence for a specific interaction of the carbenium ion with the n-donor substituent, which becomes evident in gaseous systems, owing to the absence of competitive solvation and of specific effects of the counterion and the catalyst. By contrast, Friedel–Crafts isopropylation of the halobenzenes, carried out in nitromethane solution with propene or isopropyl bromide in the presence of $AlCl_3$ or $FeCl_3$ as the catalysts, leads predominantly to para substitution.[19]

To ascertain whether positional and substrate selectivity have a common origin, i.e., can be traced back to the same activation energy barriers on the reaction coordinate, the nature of the alkylating reagent has been changed by carrying out the radiolysis of the system in the presence of i-C_3H_7Cl.

In fact, diisopropylchloronium ions are expected to form from the reaction of sec-$C_3H_7^+$ with isopropyl chloride[20] and are likely to be milder alkylating species than the free isopropyl cations. Accordingly, the data of Table II show a sharp decrease in the alkylation rate of chlorobenzene, relative to toluene, without a corresponding depression of the yields of chlorocumenes, even in the presence of a large excess of isopropyl chloride (21.5 Torr with respect to 1.2 Torr of PhCl). This indicates that $(C_3H_7)_2Cl^+$ ions can alkylate chlorobenzene as well, and suggests that the heat of formation of the condensation adduct between the aromatic substrate and the isopropyl cation is comparable to, if lower than, that of the diisopropychloronium ion.

On the other hand, the isomeric composition of the halocumenes and of the cymenes, from the experiments in the presence of isopropyl chloride, appears fully comparable with that outcoming from the reaction of free sec-$C_3H_7^+$ cations, which indicates that positional selectivity is determined by the same factors in both cases.

The apparently conflicting evidence of increased substrate discrimination and constant isomeric composition of products from the reaction of a milder electrophile lends a certain support to the hypothesis that substrate reactivity is determined at an earlier stage, i.e., formation of the condensation adduct, than positional selectivity, which depends, instead, on the relative heights of the activation energy barriers to pass from this adduct to the isomeric haloarenium ions I.

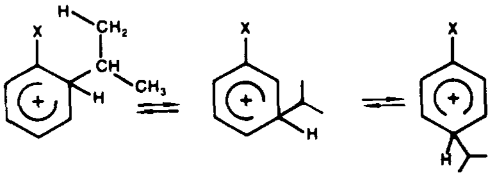
Both the isomeric composition of the halocumenes, as illustrated in Figure 1, and the relative alkylation rates, as shown in Tables I-III, depend on the pressure of the system.

The composition of isopropylated products from all substrates is shifted in favor of the meta isomer by lowering the pressure, indicating a progressive change of the regioselectivity of the substitution from apparent kinetic control, i.e., ortho, to thermodynamic control, i.e., meta.

This can be explained with increasing isomerization (4) of the haloarenium ions I, excited by the exothermicity of the condensation reaction (2), toward the equilibrium composition, as the efficiency of collisional deactivation is lowered with the pressure of the system.

In this connection it is interesting to point out that the isomeric composition of the halocumenes found at equilibrium in solution,[21] i.e., F = 22% ortho, 62% meta, 16% para; Cl = 10% ortho, 66% meta, 24% para; Br = 9% ortho, 66% meta, 25% para, while going in the same direction—high meta substitution—is somewhat different from that measured in the gas phase at 20 Torr.

This can be understood (1) owing to the solvation and counterion effects which can affect the free-energy differences among the haloarenium ion isomers (Ia, Ib, and Ic), and therefore their equilibrium composition in solution, and (2) as probably equilibrium is not yet attained in the gas phase, at the lowest pressure investigated.



(4)

Ia Ib Ic

As shown in Tables I-III, the product composition change with the pressure is coupled with an apparent increase of the alkylation rate of the halobenzenes, relative to toluene. This is particularly evident below 100 Torr, and has been observed also in benzene/toluene competitions,[22] where the variation of partial rate factors[23] suggests, along with isomerization, that the condensation adduct from toluene decomposes in part when the pressure is lowered.

Actually, the condensation of sec-$C_3H_7^+$ ions with toluene is more exothermic than with benzene and the halobenzenes, and the adduct from it should form with correspondingly higher excitation energy. Moreover, $PhCH_3$ has a higher proton affinity than the other substrates. This helps explain why its condensation adduct can more easily undergo decomposition, via reaction 5, unless efficiently stabilized by collisions.

$$[sec\text{-}C_3H_7PhCH_3]^+_{exc} \rightarrow PhCH_3{\cdot}H^+ + C_3H_6 \qquad (5)$$

In summary, the present results suggest, on one hand, that the increased relative alkylation rates of the halobenzenes at low pressure can be essentially traced to partial conversion of the excited condensation adduct from toluene into the protonated substrate. On the other hand, extensive isomerization among the excited haloarenium ions I toward a thermodynamic distribution of products, owing to decreased collision frequency with the thermal bath-gas molecules, can explain the change of the isomeric composition of products.

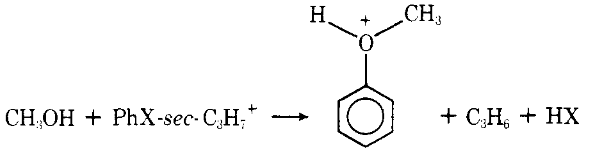
Nucleophilic Attack on the sec-$C_3H_7^+$–Halobenzene Adducts. To gather information about the structure of intermediates, the reaction has been carried out in the presence of a strong nucleophile, methanol.

As shown in Table IV, appreciable amounts of anisole were recovered, together with the alkylation products, from the halobenzenes, but not from toluene, while no detectable yield of isopropyl halide could be found. The yield of anisole, compared, for instance, to that of the corresponding halocumenes, increases with the concentration of methanol, for any given substrate.

Among the halobenzenes, the order for halogen displacement is PhF > PhCl ≃ PhBr, i.e., opposite to that expected from the direct radiolysis of the substrates, whose role can be therefore excluded on this ground as well.

Moreover, the combined yields of anisole and of the halocumenes, compared to those of cymenes, fit the substrate reactivity ratio with toluene in competitive experiments.

Hence, anisole is likely formed at the expenses of the halocumenes, i.e., it arises from the reaction of a common ionic intermediate with methanol, probably according to process 6.



(6)

II

Methylphenyloxonium ions II eventually give anisole, following proton transfer to a base.

Incidentally, a species characterized by a m/e ratio typical of ion II has been observed in the C_3H_8 CI spectrum of fluorobenzene, in the presence of methanol.[23]

Reaction 6 can be regarded as a gas-phase nucleophilic substitution by a neutral reagent (CH_3OH) on the aromatic ring, promoted by the interaction with the isopropyl cation. This situation is reminiscent of the acid and/or hydrogen-bonding catalyzed nucleophilic substitution undergone in solution by halogenated aromatics.[24]

Interestingly enough, the reactivity order for halogen displacement parallels that found by Speranza and Cacace[25] for the dehalogenation of the halobenzenes, promoted by strong gaseous Brønsted acids as CH_5^+ and $C_2H_5^{5+}$. In that case, of course, the energetics of the proton-transfer reaction to the halogen substituent allowed formation of $C_6H_5^+$ ions, following hydrogen halide elimination, while in the present experiments protonation at the halogen of the phenyl halides should be prevented on thermochemical grounds.

On the contrary, the yields of methyl halides from the reaction of decay-produced methyl cations with the halobenzenes indicate formation of methylphenylhalonium ions both in the liquid and in the gaseous phase, following the order $CH_3Br \gg CH_3Cl > CH_3F$.[26]

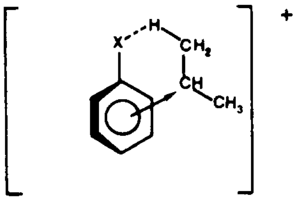
These observations suggest a different reactivity order for the attack of electrophilic carbon and hydrogen toward the halogen atom of the halobenzenes, the present results following the latter.

This analogy, and especially the failure to observe any isoprophyl halide as a leaving group, suggests that the substrates are activated toward nucleophilic displacement by the interaction of the substituent with one hydrogen atom of the isopropyl cation.

Independent, albeit indirect, support to this view is provided by Jorgensen's calculations,[27] showing that the lowest energy minimum for protonated isopropyl chloride corresponds to a structure where chlorine coordinates with both carbonium carbon and hydrogen of the isopropyl groups.

Moreover, evidence does exist in favor of bonding interactions between the Cl atom and hydrogens on the carbon β to chlorine for the dialkylchloronium ions as well.[20]

In the present case, the π electrons available from the aromatic ring are expected to participate in bonding as well, so that the isopropyl cation might be represented as "chelating" the halobenzene, as schematically depicted in structure III.



III

This structure, of course, is simply proposed as an intuitive drawing justifying the observed kinetic phenomena, and has by no means been characterized directly.

At any rate, independently of its structure, the ionic intermediate postulated for nucleophilic substitution must be stable enough to survive some 100 unreactive collisions, before encountering the nucleophile. This is due to the composition of the system, which contains propane in large excess (720 Torr) over methanol (4-6 Torr).

It therefore appears, as suggested before, that both nucleophilic and electrophilic substitution pathways pass through a common energy minimum, corresponding to the *sec*-$C_3H_7^+$-halobenzene adduct. The rate of formation of this intermediate determines the reactivity order of the substrates, which is the same for both processes.

The positional selectivity of the electrophilic substitution, instead, is subsequently controlled by the conversion of the condensation adduct into the arenium ions (I).

Since it does not necessarily involve breaking of the interaction between the carbenium ion and the ring substituent, the formation of the ortho isomer appears kinetically favored when the condensation adduct is readily deactivated by collisional quenching. Increasing isomerization among the arenium ions takes place toward thermodynamic control of products as the pressure is lowered.

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