

mmol) of palladium(II) chloride, and 13.44 g (100.0 mmol) of cupric chloride in 75 ml of methanol was allowed to react with carbon monoxide (3 atm) for 72 h at room temperature. Before depressurization, the reaction vessel was cooled to ~ -10 °C by immersion in an ice-salt bath. The pressure was then released slowly and the cold mixture was transferred immediately to a fractional distillation apparatus. The temperature of the reaction mixture was raised slowly to 60° and the low-boiling distillate collected in a tared trap surrounded by a dry ice-2-propanol bath. This procedure afforded 0.82 g of a liquid which was shown by VPC analysis on the FFAP column to contain two components. The components, in order of elution, were identified as methyl formate (50% of the peak area) and methanol (50%). These results were confirmed by ^1H NMR analysis and suggest that a minimum yield of 14% (7 mmol) of methyl formate based on copper(II) was formed. The usual work-up which followed provided a 60% yield based on copper(II) of β -methoxy ester as determined by VPC analysis.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for partial support of this research.

References and Notes

- (1) For a preliminary report of this work, see J. K. Stille, L. F. Hines, R. W. Fries, P. K. Wong, D. E. James, and K. Lau, *Adv. Chem. Ser.*, **No. 132**, 90 (1974).
- (2) Abstracted in part from the Ph.D. thesis of D. E. James, University of Iowa, Iowa City, Iowa, May 1975.
- (3) D. M. Fenton, U.S. Patent 3 397 226 (1968); *Chem. Abstr.*, **69**, 66919n (1968).
- (4) J. Tsuji and H. Takahashi, Japanese Patent 15 165 (1968); *Chem. Abstr.*, **70**, 67653d (1969).
- (5) G. Biale, U.S. Patent 3 530 168 (1970).
- (6) D. M. Fenton and P. J. Steinwand, *J. Org. Chem.*, **37**, 2034 (1972).
- (7) R. F. Heck, *J. Am. Chem. Soc.*, **94**, 2712 (1972).
- (8) D. E. James, L. F. Hines, and J. K. Stille, *J. Am. Chem. Soc.*, preceding paper in this issue.
- (9) F. C. Phillips, *Am. Chem. J.*, **16**, 255 (1894).
- (10) W. G. Lloyd and D. R. Rowe, *Environ. Sci. Technol.*, **5**, 1133 (1971).
- (11) G. Bauer, "Handbook of Preparative Inorganic Chemistry", Academic Press, New York, N.Y., 1965, p 1008.
- (12) W. G. Lloyd, *J. Org. Chem.*, **32**, 2816 (1967).
- (13) M. Graziana, P. Uguagliata, and G. Carturan, *J. Organomet. Chem.*, **27**, 275 (1971).
- (14) M. Hidai, M. Kokura, and Y. Uchida, *J. Organomet. Chem.*, **52**, 431 (1973).
- (15) G. Minghetti, F. Bonati, and G. Banditelli, *Synth. Inorg. Met.-Org. Chem.*, **3**, 415 (1973).
- (16) D. M. Barlex and R. D. W. Kemmitt, *J. Chem. Soc., Dalton Trans.*, 1436 (1972).
- (17) A. Vitagliano, *J. Organomet. Chem.*, **81**, 261 (1974).
- (18) C. H. Brubaker and M. Wicholas, *J. Inorg. Nucl. Chem.*, **27**, 59 (1965).
- (19) A. G. Massey, "Comprehensive Inorganic Chemistry", Vol. 3, A. F. Trotman-Dickenson, Ed., Pergamon Press, Oxford, 1973, pp 60-62.
- (20) J. F. Weiss, G. Tollin, and J. T. Yoke, *Inorg. Chem.*, **3**, 1344 (1964).
- (21) I. Wender, S. Metlin, E. Ergun, H. W. Sternberg, and H. Greenfeld, *J. Am. Chem. Soc.*, **78**, 5401 (1956).
- (22) H. C. Brown, "Hydroboration", W. A. Benjamin, New York, N.Y., 1962, pp 198-202.
- (23) A. S. Hussey, R. H. Baker, and G. W. Kœulks, *J. Catal.*, **10**, 258 (1968).
- (24) R. F. Heck, *J. Am. Chem. Soc.*, **93**, 6896 (1971).
- (25) F. R. Hartley, *Chem. Rev.*, **73**, 163 (1973).
- (26) F. Conti, L. Raimondi, and G. F. Pregaglia, *J. Organomet. Chem.*, **70**, 107 (1974).
- (27) J. Falbe, N. Huppès, and F. Korte, *Chem. Ber.*, **97**, 863 (1964).
- (28) R. Lai and E. Ucciani, *Adv. Chem. Ser.*, **No. 132**, 1 (1974).
- (29) H. C. Volger, *Am. Chem. Soc., Div. Pet. Chem., Prepr.*, **14**, 372 (1969).
- (30) P. P. Nicholas, C. J. Carman, A. R. Tarpley, and J. H. Goldstein, *J. Phys. Chem.*, **76**, 2877 (1972).
- (31) R. L. Pescok in "Principles and Practice of Gas Chromatography", R. L. Pescok, Ed., Wiley, London, 1959, Chapter 13.
- (32) R. A. McKenna and J. A. Idlemann, *Anal. Chem.*, **31**, 2000 (1959).
- (33) A. I. Vogel, "Practical Organic Chemistry", 3rd ed, Wiley, New York, N.Y., 1956.
- (34) H. LeMoal, A. Foucaud, R. Carrie, J. Hamelin, and C. Sevellac, *Bull. Soc. Chim. Fr.*, **3**, 579 (1964).
- (35) A. Fredga and U. Sahlberg, *Ark. Kemi, Mineral. Geol. A18*, **16**, 8 (1944).
- (36) V. C. Barry and D. Twomey, *Proc. R. Ir. Acad., Sect. B*, **51**, 137 (1947).
- (37) H. Wren and H. Williams, *J. Chem. Soc.*, **109**, 572, (1916).
- (38) P. K. Wong and J. K. Stille, *J. Org. Chem.*, **40**, 335 (1975).
- (39) L. F. Hines and J. K. Stille, *J. Am. Chem. Soc.*, **94**, 485 (1972).
- (40) K. Alder and G. Stein, *Justus Liebigs Ann. Chem.*, **504**, 216 (1933).
- (41) E. J. Eisenbraun, P. G. Hanel, K. S. Schorno, St. F. Dilgen, and J. Osiecki, *J. Org. Chem.*, **32**, 3010 (1967).
- (42) S. F. Birch, W. J. Oldham, and E. A. Johnson, *J. Chem. Soc.*, 818 (1947).
- (43) H. A. Smith and F. P. Byrne, *J. Am. Chem. Soc.*, **72**, 4406 (1950).
- (44) H. R. Snyder and R. E. Putnam, *J. Am. Chem. Soc.*, **76**, 33 (1954).
- (45) J. M. Osbond, *J. Chem. Soc.*, 4785 (1952).
- (46) D. Klamann and W. Lache, *Brennst.-Chem.*, **45**, 33 (1964).
- (47) G. P. Schlemenz and H. Engelhard, *Chem. Ber.*, **95**, 195 (1962).
- (48) R. A. Benkeser, J. Hooz, T. V. Liston, and A. E. Trevillyan, *J. Am. Chem. Soc.*, **85**, 3984 (1963).

Gas-Phase Alkylation of Xylenes by $t\text{-C}_4\text{H}_9^+$ Ions

Pierluigi Giacomello* and Fulvio Cacace

Contribution from the University of Rome, 00100 Rome, Italy. Received May 20, 1975

Abstract: The gas-phase alkylation of xylenes by $t\text{-C}_4\text{H}_9^+$ ions from the radiolysis of neopentane has been investigated in the pressure range from 20 to 771 Torr. The gaseous cation is entirely unreactive toward *p*-xylene and alkylates *o*-xylene, yielding exclusively 1,2-dimethyl-4-*tert*-butylbenzene. Reaction with *m*-xylene yields a mixture of 1,3-dimethyl-4-*tert*-butylbenzene and 1,3-dimethyl-5-*tert*-butylbenzene, whose isomeric ratio depends on the experimental conditions, ranging from the 8:92 value observed at 20 Torr in the absence of added bases to the 89:11 value measured at 770 Torr in the presence of NH_3 . The *substrate* selectivity of the gaseous electrophile has been studied by competition experiments with respect to toluene. The observed $k_{o\text{-xylene}}:k_{\text{toluene}}$ ratio of 2.0 ± 0.2 appears fairly independent of the experimental conditions, while the apparent $k_{m\text{-xylene}}:k_{\text{toluene}}$ ratio is considerably affected by the nature and the concentration of gaseous bases, ranging from 0.65 ± 0.1 in the absence of NH_3 to 1.9 ± 0.2 in the presence of excess NH_3 . These results are interpreted assuming the reversible *tert*-butylation at the ring positions ortho to one methyl group of *m*-xylene in order to explain both the effect of the pressure and of NH_3 on the isomeric composition of products and the apparent changes of the reactivity of *m*-xylene with respect to that of toluene. The reaction provides an example of an aromatic alkylation by a gaseous, unsolvated carbenium ion and allows the direct evaluation of the reactivity and the steric requirements of the electrophile, unaffected by the complicating effects of the solvent and the counterion invariably present in solution. The unusual *substrate* and *positional* selectivity of the gaseous $t\text{-C}_4\text{H}_9^+$ reagent, in particular the remarkable extent of the substitution ortho to one methyl group of *m*-xylene, are discussed in comparison with the conventional Friedel-Crafts alkylation.

The extension of the classical kinetic methods of solution chemistry to the gas-phase ionic reactions has been recently undertaken by new experimental approaches¹⁻³ that allow

the actual isolation of the reaction products and the determination of their structure and isomeric composition.

Previous investigations on the reactivity of gaseous cat-

ions toward aromatic substrates⁴⁻¹⁰ led to the demonstration of a remarkable *substrate* and *positional* selectivity of the gaseous $t\text{-C}_4\text{H}_9^+$ ion in its electrophilic attack on benzene and toluene.¹¹

The considerable interest attached to directive effects in the aromatic substitutions occurring in the gas phase, i.e., in the absence of solvation, ion pairing, etc., has stimulated further work, especially in the direction of assessing the *intrinsic* steric requirements of the $t\text{-C}_4\text{H}_9^+$ cation, traditionally regarded as a "bulky" electrophile, in the absence of solvation. This paper describes the extension of the investigation to the gas-phase alkylation of the xylenes by radiolytically formed $t\text{-C}_4\text{H}_9^+$ ions in order to evaluate the general reactivity of the electrophile and, in particular, its *substrate* and *positional* selectivity.

Experimental Section

Materials. Toluene and *o*-, *m*-, and *p*-xylene were gas chromatographic standards from C. Erba Co., and their analysis, carried out by GLC on the same columns used for the separation of the reaction products, showed an impurities content below 0.2% and the absence of the corresponding *tert*-butylated products. The samples of xylenes used in competition experiments revealed a content of undesired isomeric dimethylbenzenes below 0.1% and ca. 20 ppm of toluene. The authentic samples of the alkylation products from toluene were the same as in a previous work,¹¹ as well as the neopentane (Research Grade from Matheson Co., with a purity exceeding 99 mol %), the methane, and the oxygen (from Caracciolo-ossigeno Co.). 1,2-Dimethyl-4-*tert*-butylbenzene and 1,3-dimethyl-5-*tert*-butylbenzene were prepared from the reaction of the appropriate xylene with *tert*-butyl chloride on AlCl_3 at room temperature and were purified by preparative GLC with a 4-m E-301 Silicone oil column. 1,3-Dimethyl-4-*tert*-butylbenzene¹³ and 1,4-dimethyl-2-*tert*-butylbenzene¹⁴ were prepared from the appropriate xylene isomer and *tert*-butyl alcohol in 80% H_2SO_4 at room temperature. All compounds used were Research Grade reagents from Merck Co. The samples were further purified by GLC on a 4-m E-301 Silicone oil column and/or on a 8-m Apiezon "L" grease column. The identity of all standards was further confirmed by NMR spectroscopy. The preparation of 1,2-dimethyl-3-*tert*-butylbenzene and 1,3-dimethyl-2-*tert*-butylbenzene standards was not attempted, as their formation in the alkylation experiments was deemed unlikely. In any case, their boiling points are presumably higher than those of the less crowded isomers (for a comparison, see the corresponding trimethylbenzene isomers) and their retention times on a Apiezon "L" grease column correspondingly higher.

Other peaks, but those unequivocally identified, were not detected during the analyses within the range of retention volumes comparable with that expected for the two last isomers quoted.

Procedure. The gaseous samples were prepared by conventional techniques using a greaseless vacuum line. Reaction vessels were break-seal tipped Pyrex bulbs of 500–1000-ml volume or cylindrical containers having a capacity from 20 to 150 ml. After sealing to the vacuum line and careful degassing, they were filled to the desired pressure with reagents previously dried over 50-cm columns containing activated 5 Å molecular sieves, then cooled to the liquid nitrogen temperature and sealed off. Irradiations were carried out in a cobalt-60 220 GAMMACELL from Nuclear Canada Ltd. at a dose rate of $5.8 \times 10^5 \text{ rad h}^{-1}$ as determined by a Fricke dosimeter at a temperature of ca. 37.5 °C.

Products analyses were performed with a C. Erba Model 2400 T or a Hewlett-Packard 5700 A gas chromatograph, equipped with flame ionization detectors, by injecting known aliquots of the homogeneous gas phase contained in the reaction bulbs. Analytical $\frac{1}{8}$ in. o.d. stainless steel columns were used at temperatures from 80 to 150 °C, and the identity of the alkylation products was established by comparison of their retention volumes on at least two different columns with those of authentic samples. The yields were measured by integration of the peak areas using individual calibration curves for each product. The following columns were used: 4-m 25% Apiezon "L" grease, 4-m 15% tricresyl phosphate, 4-m 10% poly(propylene glycol) (UCON-LB 550), 2.5-m 20% Bentone 34/diisodecyl phthalate (8:10). All the liquid phases were ad-

sorbed on 60–80 mesh Chromosorb W.

The alkylation has been carried out by irradiating a homogeneous gaseous system containing neopentane as the bulk constituent in the presence of traces of the aromatic substrate(s), of a radical scavenger (O_2), and of a gaseous base (ethanol, *tert*-butyl alcohol, or NH_3), with the ^{60}Co γ radiation at doses ranging from 0.7 to 12 Mrad.

The gas-phase proto-de-*tert*-butylation of 1,3-dimethyl-4-*tert*-butylbenzene was studied with an analogous technique by irradiating a gaseous system containing a few torr of the substrate and a large excess of CH_4 , in the presence of O_2 , used as a radical scavenger. The irradiations were performed in Pyrex bulbs at doses of 2–9 Mrad, and the analysis of the reaction products was carried out on the same columns described above.

Relative yields from the analysis of different samples from the same reaction vessel were reproduced with an accuracy of 1%. Reported deviations of ca. 5% refer to the scattering of data from the mean of several experiments and are mainly due to difficulties in reproducing the composition of the system.

Results

The composition of the systems irradiated and the *relative* yields of the products formed from *o*-, *p*-, and *m*-xylene are given respectively in Tables I to III.

The *absolute* yields, i.e., the ratio of the alkylated products to the total $t\text{-C}_4\text{H}_9^+$ ions formed from the radiolysis of neopentane, are largely variable (3 to 60%) and of limited significance, since the aromatic substrate, contained in traces in the gas, represents only one of the nucleophiles competing for the $t\text{-C}_4\text{H}_9^+$ reagent. In general, yields increase with the molar fraction of the substrate and decrease with the concentration of any added bases or with the radiation dose, i.e., with the concentration of radiolytically formed nucleophiles. Nevertheless, the results of the competition experiments indicate that, for any given initial composition of the system, the ratio of the apparent k values of the substrates is reasonably constant, suggesting that parasitic reactions of $t\text{-C}_4\text{H}_9^+$ ions with nucleophiles other than arenes, either deliberately added to the system or formed during the radiolysis, while decreasing the absolute yields do not interfere to a different extent with the competing alkylation processes of the two aromatic substrates.

In addition, it should be noted that the absolute yields, measured in separated irradiations carried out under comparable conditions, of systems having the same composition are reasonably constant. Thus, irradiation of three equal samples, containing neopentane (720 Torr), *o*-xylene (1.0 Torr), and ethanol (0.34 Torr) with a dose of 8.7 Mrad, gave absolute yield values of 2.0, 2.6, and 3.2%, respectively.

From Table I it is apparent that alkylation of *o*-xylene yields exclusively 1,2-dimethyl-4-*tert*-butylbenzene and that the apparent $k_{o\text{-xylene}}:k_{\text{toluene}}$ ratio is fairly independent of the experimental conditions, ranging from 1.7 to 2.3. No alkylated products from *p*-xylene could be detected, as shown in Table II. The isomeric composition of the products from *m*-xylene depends markedly on the nature and the concentration of the bases added to the gas, as illustrated in Table III, and on the pressure of the gaseous system, as shown in Table IV and Figure 1, which refer to experiments carried out without added bases. The apparent $k_{m\text{-xylene}}:k_{\text{toluene}}$ ratio is also significantly affected by the concentration of bases ranging from 0.5 to 1.9, the highest value being measured in systems containing the largest excess of NH_3 . Direct competition experiments carried out in the absence of NH_3 led to an apparent $k_{o\text{-xylene}}:k_{m\text{-xylene}}$ ratio ranging from 2.5 at 720 Torr to 2.0 at 43 Torr.

Discussion

The gaseous electrophile used in the present work is the relatively stable¹⁵ $t\text{-C}_4\text{H}_9^+$ cation, generated in the gas

Table I. Gas-Phase *tert*-Butylation of *o*-Xylene and Toluene

Composition of gaseous system, ^a Torr					Isomeric composition of products, ^b %				
Neopentane	Substrates		O ₂	Added base	<i>k</i> _{<i>o</i>-xylene} <i>k</i> _{toluene}	<i>tert</i> -Butylxylenes		<i>tert</i> -Butyltoluenes	
	<i>o</i> -X	T				1,2,4	1,3	1,4	
765	1.27		5			100			
720	1.00		10	EtOH, 0.34		100			
761	0.54		5	EtOH, 1.01		100			
204	0.74		3			100			
48	0.46		2			100			
735	1.09	1.40	6		1.8	100	6		94
97	0.24	0.20	3		1.7	100	25		75
732	0.69	1.12	7		1.7	100	9		91
732	0.69	1.12	7		1.8	100	8		92
732	0.69	1.12	7		1.8	100	7		93
732	0.69	1.12	7		1.7	100	8		92
748	1.06	0.76	5	EtOH, 2.03	2.1	100	6		94
750	1.76	0.61	5	EtOH, 0.41	2.3	100	7		93
750	0.037	0.55	5	EtOH, 0.51	2.0	100	7		93
708	1.50	1.80	10	NH ₃ , 45	2.2	100	5		95

^a *o*-X for *o*-xylene, T for toluene. ^b Standard deviation of data ca. 5%. Position of *tert*-butyl group italicized.

Table II. Gas-Phase *tert*-Butylation of *p*-Xylene and Toluene

Composition of gaseous system, ^a Torr					Isomeric composition of products, ^b %		
Neopentane	Substrates		O ₂	Added base	<i>k</i> _{<i>p</i>-xylene} <i>k</i> _{toluene}	<i>tert</i> -Butyltoluenes	
	<i>p</i> -X	T				1,3	1,4
725	1.40		2			Below detection limit	
750	3.07		7			Below detection limit	
756	1.65	1.03	7	EtOH, 4.1		4	96
680	1.70	1.40	10	NH ₃ , 45		5	95

^a *p*-X for *p*-xylene, T for toluene. ^b Detection limit, ca. 0.01% of the starting arene. Standard deviation of data ca. 5%. Position of *tert*-butyl group italicized.

Table III. Competitive Gas-Phase *tert*-Butylation of *m*-Xylene and Toluene

Composition of gaseous system, ^a Torr					Isomeric composition of products, ^b %				
Neopentane	Substrates		O ₂	Added base	<i>k</i> _{<i>m</i>-xylene} <i>k</i> _{toluene}	<i>tert</i> -Butylxylenes		<i>tert</i> -Butyltoluenes	
	<i>m</i> -X	T				1,3,4	1,3,5	1,3	1,4
725	1.25		1			65	35		
734	0.90		7	EtOH, 1.10		65	35		
734	0.95	1.12	7	EtOH, 1.10	0.7	65	35	6	94
750	0.61	2.14	5	EtOH, 1.14	0.7	54	46	9	91
745	1.00	2.1	7	EtOH, 22.3	0.8	69	31	5	95
750	0.06	0.6	5	EtOH, 1.12	0.6	53	47	6	94
720	0.72	1.21	7	<i>t</i> -BuOH, 0.36	0.6	63	37	7	93
720	1.00	1.30	7	NH ₃ , 0.07	0.5	76	24	7	93
720	0.87	1.56	7	NH ₃ , 7.6	1.6	87	13	6	94
690	1.20	1.50	7	NH ₃ , 70	1.9	89	11	4	96

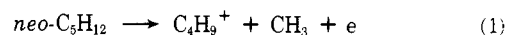
^a *m*-X for *m*-xylene, T for toluene. ^b Standard deviation of data ca 5%. Position of *tert*-butyl group italicized.

Table IV. Pressure Dependence of the Isomeric Composition of Products from the *tert*-Butylation of *m*-Xylene

System composition, Torr			Rel yields ^a of dimethyl- <i>tert</i> -butylbenzenes, %	
Neopentane	<i>m</i> -Xylene	O ₂	1,3,4	1,3,5
20	0.63	1	8	92
40	0.55	5	8	92
100	0.64	2	9	91
200	0.71	2	28	72
300	0.64	2	40	60
400	0.69	2	50	50
500	0.39	3	56	44
725	1.25	1	65	35

^a Position of *tert*-butyl group italicized.

phase from the radiolysis of neopentane



and thermolyzed by a large number of unreactive¹⁶ collisions with the neopentane molecules, according to a technique first developed by Ausloos and coworkers¹⁷ and subsequently applied to the study of gas-phase aromatic substitutions.⁹⁻¹² The basic features of this technique and the choice of the experimental conditions necessary to ensure a unique path for the formation of the alkylated products have been discussed in detail elsewhere.¹¹ The conditions typical of the present experiments, in particular the low concentrations of aromatic substrate(s), the high concentrations of an effective radical scavenger, the observed constancy of the relative yields over an extended dose range,

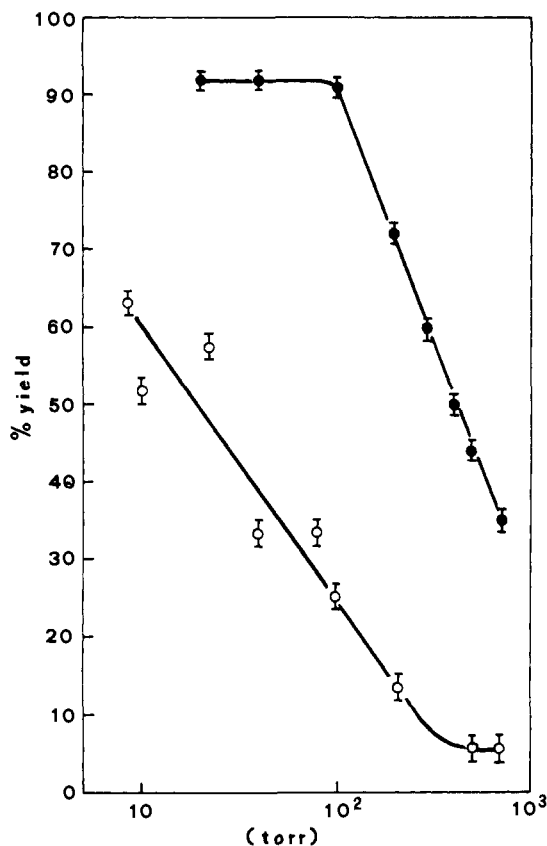
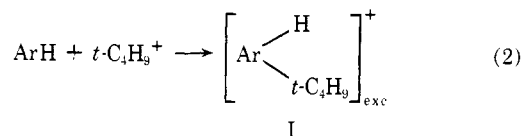


Figure 1. Dependence of the relative yields of 1,3-dimethyl-5-*tert*-butylbenzene (●) and of *m*-*tert*-butyltoluene (○) on neopentane pressure.

ensure that the electrophilic attack of thermal *tert*-butyl ions on the aromatic substrate represents the only significant route to the alkylated xylenes and that parasitic processes, including radical reactions and direct radiolysis of the aromatics, can be safely disregarded.

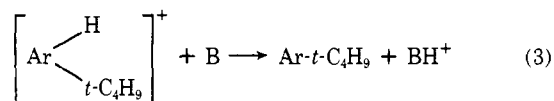
In analogy with earlier conclusions,¹⁸ it is suggested that the alkylation proceeds in the gas phase via a two-step mechanism involving the attack of the carbenium ion on the



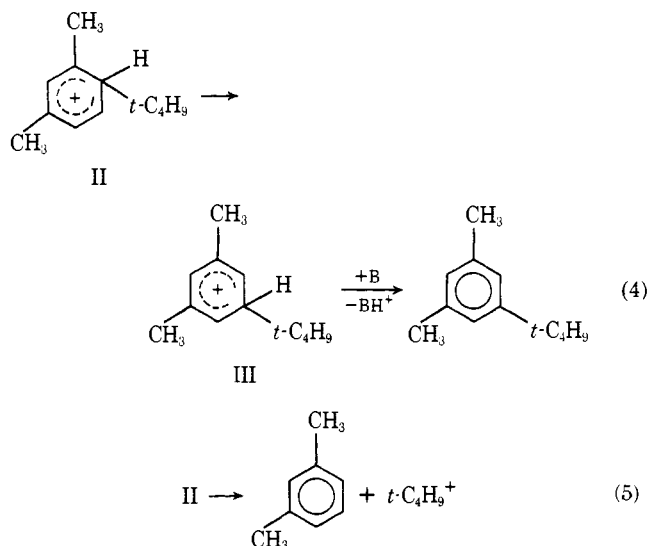
aromatic substrate, leading to the formation of a substituted arenium ion, excited by the exothermicity of the reaction. Lack of thermochemical data on the ΔH_f° values of the isomeric dimethyl-*tert*-butylarenium ions prevents precise calculations of the enthalpy changes associated with reaction 2. However, taking into account the thermoneutral or slightly endothermic character of the attack of $t\text{-C}_4\text{H}_9^+$ on benzene¹¹ and the stabilizing effect of the two methyl groups in the arenium ions (I) reflected, inter alia, by the higher PA of xylenes with respect to benzene^{19,20} (ca. 188 vs. 178 kcal mol⁻¹), the ΔH° value of process 2 and consequently the excitation energy of intermediates I can be roughly estimated to be between 10 and 15 kcal mol⁻¹.

The arenium ions, stabilized by collisions with neopentane molecules, can subsequently undergo deprotonation by an appropriate gaseous base, either deliberately added to the system or formed from its radiolysis,²¹ leading to the formation of the observed alkylated products (eq 3).

The formation of the arenium ions in an excited state is significant in connection with their possible isomerization before quenching by reaction 3.



Indeed, at least in the alkylation of *m*-xylene, the simple mechanism outlined in eq 2 and 3 is complicated by the occurrence of extensive isomerization of 1,3-dimethyl-4-*tert*-butylbenzene, that represents the major product under kinetically controlled conditions, to the thermodynamically more stable 1,3-dimethyl-5-*tert*-butyl isomer. Isomerization can conceivably occur via two different channels, involving, respectively, the *intramolecular* shift of the $t\text{-C}_4\text{H}_9$ group (eq 4) and/or its reversible dealkylation to *m*-xylene (eq 5).



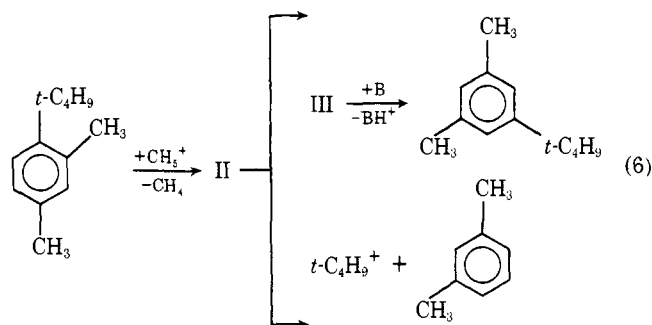
The observed dependence of the isomeric composition of products on the pressure and on the concentration of bases does not allow one, per se, to discriminate between mechanisms 4 and 5, since both intra- and intermolecular isomerization can be expected to be reduced by collisional stabilization and to increase with the lifetime of II before its quenching by reaction 3.

However, the observed increase of the apparent $k_{m\text{-xylene}}:k_{\text{toluene}}$ ratio at high concentrations of NH_3 is only consistent with mechanism 5, where fast deprotonation of II can be expected to prevent dealkylation, thus increasing the yields of *tert*-butylated arenes.

The simultaneous change of product composition and of apparent reactivity of *m*-xylene provides quantitative support to the "intermolecular isomerization" pathway, in fact; assuming that the decrease of the $k_{m\text{-xylene}}:k_{\text{toluene}}$ ratio from the 1.9 value measured at high NH_3 concentrations to the 0.6 value measured in the absence of NH_3 is due exclusively to de-*tert*-butylation of II, one can calculate that the percentage of 1,3-dimethyl-4-*tert*-butylbenzene should concurrently drop from 89%, observed at high NH_3 concentrations, to 65%, in excellent agreement with the experimental $62 \pm 6\%$ value.

In any event, in order to assess the relative rate of the two possible isomerization pathways, 1,3-dimethyl-4-*tert*-butylbenzene was protonated in the gas phase with CH_5^+ ions from the radiolysis of methane,²² measuring the relative yields of 1,3-dimethyl-5-*tert*-butylbenzene, formed in this case exclusively via intramolecular isomerization of II, and of *m*-xylene from proto-dealkylation (eq 6).

The results indicate that, over the extended range of pressure investigated (90 to 750 Torr), the yield of *m*-xylene exceeds that of 1,3-dimethyl-5-*tert*-butylbenzene by a factor of over 25:1, suggesting a much greater rate of proto-deal-



kylation with respect to intramolecular isomerization. In this connection, it should be noted that extensive proto-*tert*-butylation of methyl-*tert*-butylbenzene has been observed by Munson and Field in their study on chemical ionization of arenes by CH_5^+ and C_2H_5^+ ions.^{23,24}

Owing to the different reaction environment and especially to the higher exothermicity of (6), exceeding that of (2) by some 50 kcal mol^{-1} ,²⁵ considerable caution is required when applying the results obtained in the protonation with CH_5^+ to the alkylation with $t\text{-C}_4\text{H}_9^+$. However, since the higher excitation of the arenium ion II obtained from protonation should, in fact, make the competition between intramolecular isomerization and dealkylation less unfavorable to the process characterized by the higher activation energy, the evidence from CH_5^+ protonation strongly suggests that, as long as ortho *tert*-butylation of *m*-xylene is concerned, dealkylation of the substituted arenium ion is the predominant pathway and determines to a significant extent both the apparent reactivity of the substrate and the isomeric composition of products.

Accordingly, it appears that kinetically significant relative k values can be measured only in the presence of high concentrations of NH_3 , which prevents reversible dealkylation (and possibly transalkylation) processes.

The lack of ortho-substituted products from toluene and *o*- and *p*-xylene is to be traced to the comparatively low rate of the electrophilic attack to their insufficiently activated (vide infra) ortho positions rather than to secondary dealkylation, as shown by the failure to detect ortho-substituted products from these substrates, even under the conditions (high neopentane pressures and ammonia concentrations) that do effectively prevent reversible dealkylation in the case of *m*-xylene.

Neopentane pressure has a different effect on the isomeric composition of products from *m*-xylene and from the other substrates, e.g., toluene, as illustrated in Figure 1. The yield of 1,3-dimethyl-5-*tert*-butylbenzene, the thermodynamically most stable product from *m*-xylene, becomes constant and practically quantitative at pressures below 100 Torr, while the proportion of 3-*tert*-butyltoluene monotonically increases as the pressure is reduced to the lowest value investigated (8.7 Torr).¹¹

The different effects of pressures can be rationalized taking into account the higher exothermicity (and consequently the higher excitation energy of the arenium ions formed) in the $t\text{-C}_4\text{H}_9^+$ attack on *m*-xylene, the different isomerization mechanism, and the different effects of radiolytically formed bases (H_2O , alcohols, etc.) on the rate of deprotonation of the arenium ions from *m*-xylene and, respectively, from toluene.

As a whole, the above considerations suggest that the steric requirements of the "bulky" $t\text{-C}_4\text{H}_9^+$ reagent can affect the isomeric composition of products at two distinct stages, i.e., in the electrophilic attack (2) for all substrates and in the subsequent deprotonation step (3) for the particular case of *m*-xylene. Concerning the positional selectivity of the attack, the results can be summarized as follows. (i) Ac-

tivation of a ring position by one ortho methyl group is insufficient to balance steric hindrance. Thus, no appreciable attack does occur to the ortho positions of toluene. (ii) Activation by one ortho and one meta methyl groups is also insufficient, preventing appreciable attack of $t\text{-C}_4\text{H}_9^+$ to the ortho positions of *o*- and *p*-xylene. (iii) The combined activating effects of two methyl groups, respectively ortho and para to a given ring position, overcome the steric requirements of the reagent, conferring to the position a reactivity comparable, if somewhat lower, to that of the para position of toluene.

While meaningful calculations of partial rate factors and construction of gas-phase free energy correlations must await additional data, it appears that the reactivity of the individual methylbenzenes investigated toward the gaseous electrophile is essentially determined, under kinetically controlled conditions, by the number of free ring positions para to a methyl group. Thus, the reactivity of *o*- and *m*-xylene is approximately twice that of toluene, while benzene and *p*-xylene are less reactive than toluene by a factor of ca. 50 and, respectively, greater than 100.

The data so far available indicate that gas-phase *tert*-butylation is a "normal" aromatic substitution, in the sense that overall reactivity of each substrate is determined by the combined reactivities of its different ring positions.

Conclusions

A comparison of the gas-phase results with those obtained in solution is of interest, as the present investigation provides the first experimental determination of the *intrinsic* steric hindrance of the *tert*-butyl cation, and any difference in the positional selectivity measured in solution must be traced to solvation and/or ion pairing of the reagent.

The investigations of Brown and Smoot,²⁶ Schlatter and Clark,²⁷ and Olah and co-workers²⁸ have conclusively shown that *tert*-butylation cannot occur in solution ortho to a methyl group of toluene and polymethylbenzenes, irrespective of the nature of the reagent(s), the catalyst, and the solvent. In particular, alkylation of *m*-xylene with *tert*-butyl halides or isobutene, carried out with a variety of acidic catalysts in nitromethane, was found to yield exclusively 1,3-dimethyl-5-*tert*-butylbenzene.²⁸

In all cases, the lack of ortho substitution was traced to the steric hindrance offered by the methyl substituent to the bulky *tert*-butyl electrophile attacking the ortho position.

Our data show now that, in general, the steric requirements of the *tert*-butyl ion proper have been considerably overrated, as indicated by the fact that the free, unsolvated carbenium ion is actually capable of attacking a sufficiently activated ring position of polymethylbenzenes, even ortho to a methyl group. Our data provide conclusive support to the view that the alkylating agent in the liquid-phase *tert*-butylation is *not* a free carbenium ion and that the steric hindrance observed in solution studies is due to solvation and especially to the bulk of the counterion closely bound to the electrophile, as suggested by Olah on purely inductive grounds.²⁸

A close correspondence does exist between the essentially *intermolecular* isomerization mechanism of the gaseous *tert*-butylarenium ions and the *intermolecular* isomerization mechanism of the same intermediates prevailing in solution,²⁸ while the kinetic demonstration of the particularly fast dealkylation of *o*-methyl-*tert*-butylarenium ions in strong acids, with respect to their meta and para isomers,²⁹ provides a strict analogy to the conclusions reached in the present study on the special significance of reversible *tert*-butylation of the gaseous ion II.

Finally, the extensive proto-*tert*-butylation of di-

methyl-*tert*-butylbenzenes by CH_5^+ represents a gas-phase counterpart of the fast dealkylation of similar substrates promoted by strong acids and acidic catalysts.^{30,31}

Acknowledgment. The authors are indebted to Dr. P. Misiti for the γ irradiations. Work performed under Consiglio Nazionale delle Ricerche Research Grant 74.00574.03.

References and Notes

- (1) F. Cacace, *Adv. Phys. Org. Chem.*, **8**, 79 (1970).
- (2) F. Cacace in "Interactions between Ions and Molecules", P. Ausloos, Ed., Plenum Press, New York, N.Y., 1975.
- (3) P. Ausloos in "Ion-Molecule Reactions", J. L. Franklin, Ed., Plenum Press, New York, N.Y., 1970.
- (4) F. Cacace and S. Caronna, *J. Am. Chem. Soc.*, **89**, 6848 (1967).
- (5) F. Cacace and G. Perez, *J. Chem. Soc. B*, 2086 (1971).
- (6) F. Cacace, R. Cipollini, and G. Ciranni, *J. Chem. Soc. B*, 2089 (1971).
- (7) F. Cacace and G. Stöcklin, *J. Am. Chem. Soc.*, **94**, 2518 (1972).
- (8) F. Cacace, R. Cipollini, and G. Occhiucci, *J. Chem. Soc., Perkin Trans. 2*, 84 (1972).
- (9) S. Takamuku, K. Iseda, and H. Sakurai, *J. Am. Chem. Soc.*, **93**, 2420 (1971).
- (10) F. Cacace and E. Possagno, *J. Am. Chem. Soc.*, **95**, 3397 (1973).
- (11) F. Cacace and P. Giacomello, *J. Am. Chem. Soc.*, **95**, 5851 (1973).
- (12) P. Giacomello and F. Cacace, *J. Chem. Soc., Chem. Commun.*, 379 (1975).
- (13) B. V. Joffe and Tsan-Yang, *Zh. Obshch. Khim.*, **33**, 2196 (1963); cf. *Chem. Abstr.*, **59**, 13,884h (1963).
- (14) D. Nightgale and L. I. Smith, *J. Am. Chem. Soc.*, **61**, 101 (1939).
- (15) The experimental ΔH_f° of $t\text{-C}_4\text{H}_9^+$ is 169 kcal mol⁻¹, according to J. J. Solomon and F. H. Field [*J. Am. Chem. Soc.*, **95**, 4483 (1973)], while the theoretically calculated value is 163 kcal mol⁻¹, according to L. Radom, J. A. Pople, and P. v. R. Schleyer [*J. Am. Chem. Soc.*, **94**, 5935 (1972)].
- (16) S. G. Lias, R. E. Rebbert, and P. Ausloos, *J. Chem. Phys.*, **57**, 2080 (1972).
- (17) P. Ausloos and S. G. Lias, *J. Am. Chem. Soc.*, **92**, 5037 (1970), and references therein.
- (18) F. Cacace, R. Cipollini, P. Giacomello, and E. Possagno, *Gazz. Chim. Ital.*, **104**, 977 (1974).
- (19) S.-L. Chong and J. L. Franklin, *J. Am. Chem. Soc.*, **94**, 6630 (1972).
- (20) W. J. Hehre, R. T. McIver, Jr., J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 7162 (1974).
- (21) Ethanol (PA = 187 kcal mol⁻¹, according to M. S. B. Munson, 159th National Meeting of the American Chemical Society, Houston, Texas, 1970), which was found quite effective in the deprotonation of gaseous methyl-*tert*-butylarenium ions from the attack of $t\text{-C}_4\text{H}_9^+$ on toluene, is apparently uneffective in the case of the dimethyl-*tert*-butylarenium ions from *m*-xylene, whose fast deprotonation requires a stronger base like NH_3 [PA = 207 kcal mol⁻¹, according to M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, **50**, 2028 (1969)]. These observations can be rationalized taking into account the higher PA of the dimethyl-*tert*-butylbenzenes with respect to their methyl-*tert*-butyl homologues, which is likely to make the proton transfer from the correspondent arenium ions to ethanol an endothermic process.
- (22) For a review, see P. Ausloos, S. G. Lias, and A. A. Scala, *Adv. Chem. Ser.*, **No. 58**, 264 (1966).
- (23) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **89**, 1047 (1967).
- (24) F. H. Field and M. S. B. Munson, *J. Am. Chem. Soc.*, **89**, 4272 (1967).
- (25) ΔH_f° of CH_5^+ is taken 221 kcal mol⁻¹, according to W. A. Chupka and J. A. Berkowitz [*J. Chem. Phys.*, **54**, 4256 (1971)].
- (26) H. C. Brown and C. R. Smoot, *J. Am. Chem. Soc.*, **78**, 6255 (1956).
- (27) M. J. Schlatter and R. D. Clark, *J. Am. Chem. Soc.*, **75**, 3261 (1953).
- (28) G. A. Olah, S. H. Flood, and M. E. Moffat, *J. Am. Chem. Soc.*, **86**, 1060 (1964).
- (29) G. A. Olah, M. W. Meyer, and N. A. Overchuk, *J. Org. Chem.*, **29**, 2310 (1964).
- (30) D. M. Brouwer and E. L. Mackor, *Proc. Chem. Soc., London*, 147 (1964).
- (31) D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, **87**, 210 (1968).

Reaction of O(³P) Atoms with Toluene and 1-Methylcyclohexene

J. S. Gaffney, R. Atkinson, and J. N. Pitts, Jr.*

Contribution from the Department of Chemistry and Statewide Air Pollution Research Center, University of California, Riverside, California 92502. Received July 18, 1975

Abstract: The products and mechanisms of the reaction of O(³P) atoms with toluene and 1-methylcyclohexene have been investigated at 50–400 Torr total pressure over the temperature range 296–423 K. With toluene the volatile addition products observed were phenol, *o*-, *m*-, and *p*-cresol, along with CO, CH₄, C₂H₆, and a large amount of nonvolatile polymeric tar. The reaction of O(³P) atoms with 1-methylcyclohexene produced CO and the C₇H₁₂O addition product isomers 1-methyl-1,2-epoxycyclohexane, 2-methylcyclohexanone, 1-methylcyclopentencarboxaldehyde, methyl cyclopentyl ketone, 2-methyl-5-hexenal, 1-hepten-6-one, and 2-methyl-2-hexenal. These products are discussed in terms of a general mechanism for the gas-phase addition of O(³P) atoms to aromatic and cyclic unsaturated hydrocarbons.

Introduction

While much work has been carried out on the products and mechanisms of the gas-phase reactions of O(³P) atoms with simple olefins,^{1–13} mainly by Cvetanovic and coworkers,^{1–7} there are less data available for the reaction of O(³P) atoms with aromatic hydrocarbons^{5,14–18} and with cyclic olefins.^{2,5,7,13}

The product studies on the reaction of O(³P) atoms with aromatic hydrocarbons^{14–18} have shown that tar or polymer formation is extensive with the major volatile addition products being phenolic. In the case of the cyclic olefins, Cvetanovic and coworkers^{2,5,7} have reported the products obtained from the reaction of O(³P) atoms with cyclohexene and cyclopentene, the latter system being studied in detail.⁷ The major products for these compounds are the cyclic epoxide and ketone, together with ring-contracted and ring-opened isomers.

In this work, as part of an investigation into the rates and products of the reactions of O(³P) atoms with a variety of unsaturated organic compounds,^{19,20} we have studied the products obtained from the reaction of O(³P) atoms with toluene and 1-methylcyclohexene to determine the effect of aromaticity on the reaction mechanism. These compounds are not only of interest from the fundamental grounds of structure and reactivity, but also because of their possible significance in polluted atmospheres.

Experimental Section

The experimental system has been described in detail previously,^{19,20} and only the essential details will be given here. Ground-state oxygen atoms were produced by the mercury photosensitization of N₂O in a closed circulating reaction system. The volumes of the reaction and circulating systems were 4000 and 1043 cm³ for the studies on toluene and 1-methylcyclohexene, respectively. The reaction system was enclosed by a furnace whose temperature