Evaluation of the Lifetime of Gaseous Ion−Neutral Complexes. 1. A Chemical Activation Study

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Abstract: The lifetime of typical ion−neutral complexes (INC) has been evaluated by a chemical activation approach whereby gaseous INC are formed by an exothermic process that imparts them excess internal energy, raising their temperature to T_0, well above the temperature (T) of the bath gas. The hot INC can undergo either prompt reaction at T_0 or thermal reaction at T following collisional deactivation, and the branching ratio of the two processes is deduced from the composition of the products. We have investigated aromatic *tert*-butylation promoted by addition of toluenium ions to RX neutrals (R = t-C_4H_9, X = Cl, OH), a reaction that displays a marked temperature dependence of the isomeric composition of the products and, in addition, is known to occur within genuine INC. Following a preliminary study by Fourier transform ion cyclotron resonance and triple quadrupole mass spectrometry, the pressure dependence of the meta/para ratio of the *tert*-butyltoluenes formed has been investigated by the radiolytic technique in the range from 50 to 4560 Torr in CH_4, CH_3F and C_3H_8 at temperatures from 0 to 42 °C.

Introduction

The concept of ion−neutral complexes (INC), first postulated in the study of bimolecular reactions,[1−3] has found widespread application in the past two decades to help explain the unimolecular fragmentation of excited ions.[4−11] The interest in INC is currently enhanced by the growing recognition of their role in a variety of gas-phase reactions and of their potential value as generalized and extremely simplified models in many areas of ionic chemistry. In fact, INC can be thought of as being microscopic reaction "vessels" containing the ion and a neutral molecule. The presence of the latter, which plays the 2-fold role of the solvent and the reagent, has a dramatic effect in modifying the reactivity of the ion toward the pattern prevailing in solution, without introducing the manifold, theoretically intractable complications typical of condensed reaction environments.[7,12−14] At present time, the kinetic and mechanistic study of INC is severely hampered by the scarcity of data on certain key features. In particular, the data currently available on the lifetime of INC are preciously rare and in most cases are not the results of direct measurements, being instead the widely spaced limits set by instrumental constraints, such as the time window where metastable fragmentation is accessible to observation, and so on. This state of affairs is particularly unsatisfactory when the lifetime of the INC is limited by an intracomplex reaction, i.e., precisely in those cases, of great current interest, where the INC is the key intermediate in a gas-phase ionic reaction, since obviously the kinetic and mechanistic role of the complex hinges heavily on its lifetime behavior.

The situation seems to justify attempts at evaluating the lifetime of typical INC utilizing approaches capable of providing experimental results that, albeit approximate by exacting kinetic standards, substantially reduce the current orders-of-magnitude uncertainty range.

In this paper, we outline an approach based on the application of the radiolytic technique, characterized by an extended pressure range, from a few to several thousand Torr, by a wide temperature range, from 250 to 500 K, and by the positive structural and stereochemical identification of the products, especially with regard to their isomeric and isotopic composition.[15] Supporting evidence was sought utilizing Fourier transform ion cyclotron resonance (FT-ICR) and triple quadrupole (TQ) mass spectrometry.

Experimental Section

Materials. The gases were research products from Matheson Gas Products, Inc., or Aldrich Chemical Co., Inc., with a stated purity exceeding 99.95 mol % (O_2, CH_4, C_3H_8, and i-C_4H_8), whereas CH_3F, obtained from Fluorochem, Ltd., with a stated purity of 99 mol %, contained 0.15 mol % $(CH_3)_2O$ and traces of acetone, as established by GC and GC/MS. All chemicals used as reagents or reference standards in the analysis of the radiolytic products were research grade samples obtained from commercial sources or were prepared according

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[†] Università di Roma "La Sapienza".

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(1) Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347.

(2) Su, T.; Bowers, M. T. *Gas-Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; p 83.

(3) Magnera, T. F.; Kebarle, P. *Ionic Processes in the Gas Phase*; Almoster-Ferreira, M. A., Ed.; Reidel: Dordrecht, The Netherlands, 1984; p 135.

(4) McAdoo, D. J. *Mass Spectrom. Rev.* **1988**, *7*, 363.

(5) Holman, R. W.; Gross, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 3500.

(6) Kuck, D. *Mass Spectrom. Rev.* **1990**, *9*, 583.

(7) Bowen, R. D. *Acc. Chem. Res.* **1991**, *24*, 364.

(8) Longevialle, P. *Mass Spectrom. Rev.* **1992**, *11*, 157.

(9) Morton, T. H. *Org. Mass Spectrom.* **1992**, *27*, 353.

(10) McAdoo, D. J.; Morton, T. H. *Acc. Chem. Res.* **1993**, *26*, 295.

(11) Audier, H. E.; Fossey, J.; Mourgues, P.; McMahon, T.; Hammerum, S. *J. Phys. Chem.* **1996**, *100*, 18380.

(12) Berthomieu, D.; Brenner, V.; Ohanessian, G.; Denhez, J.; Millié, P.; Audier, D. H. *J. Am. Chem. Soc.* **1993**, *115*, 2505.

(13) Berthomieu, D.; Brenner, V.; Ohanessian, G.; Denhez, J. Millié, P.; Audier, D. H. *J. Phys. Chem.* **1995**, *99*, 712.

(14) Norman, K.; McMahon, T. B. *J. Am. Chem. Soc.* **1996**, *118*, 2449.

(15) Cacace, F. *Acc. Chem. Res.* **1988**, *21*, 215 and references therein.

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to standard procedures. C_6D_6 and $CD_3C_6D_5$ were obtained from Aldrich with an isotopic purity of 99.96 D atom %.

Instruments. The FT-ICR mass spectra were recorded using a Bruker Spectrospin APEX TM 47e spectrometer, equipped with an external ion source, a computer-controlled pulsed valve, and a X Mass data system. The TQ instrument was a VG Micromass model Quattro spectrometer, equipped with a CI ion source allowing direct introduction of liquid samples. The ions generated by CH_4/CI in the source at a pressure of ca. 10^{-4} Torr and mass selected by the first quadrupole were introduced into the second quadrupole, actually a hexapolar cell (RF-only) containing the neutral reagent, at pressures from 1.5×10^{-6} to 5×10^{-5} Torr, and the ionic products were analyzed in the third quadrupole utilizing a scan frequency of 150 amu s^{-1}. The radiolytic products were analyzed by using a TRIO VG Micromass benchtop GC/MS spectrometer.

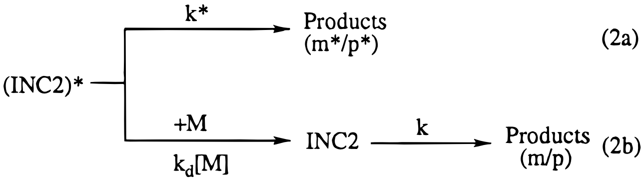
Radiolytic Experiments. The gaseous samples were prepared by standard techniques using a greaseless vacuum line in sealed 135 mL Pyrex ampules. The irradiations were performed in a 220 Gammacell (Nuclear Canada Ltd.) equipped with a thermostatic device designed to maintain the sample to within ±1 °C in the temperature range from 0 to 42 °C. The irradiation time was 2 h to the total dose of 1.0×10^4 Gy. The irradiated vessels were cooled to 77 K, and their contents dissolved into methanol, washing the inner walls and performing repeated freeze-thawing cycles. The nature, yields, and D content of the products were determined by GC/MS, making use, when required, of specifically labeled reference standards. The analyses were performed in triplicate, correcting the results for the incomplete labeling of the C_6D_6 and $CD_3C_6D_5$ reagents, and, for the ^{13}C contribution, using a 50-m long, 0.2-mm i.d. fused-silica column coated with a 0.5-mm layer of cross-linked methylsilicone (PONA column from Hewlett-Packard Co.) operated in the temperature range from 70 to 220 °C.

Methodology

We utilized the so-called "Crafts−Friedel" reactions that are positively known to proceed in the gas phase via intermediates endowed with all features typical of genuine INC, including the mutual rotation of the components as demonstrated by recent experiments involving chiral reagents.[16−19] The reaction proceeds according to the general sequence

$$ArH_2^+ + P \rightleftharpoons \underset{\text{INC1}}{[ArH_2^+\cdot P]} \rightleftharpoons \underset{\text{INC2}}{[ArH\cdot E^+]} \rightarrow \text{Products} \quad (1)$$

where ArH_2^+ denotes an arenium ion and P a proelectrophile, namely a molecule whose protonation generates the electrophile, E^+. We focused attention on *tert*-butylation, one of the most thoroughly studied and best understood ionic gas-phase alkylations,[20−28] utilizing *tert*-butyl alcohol, *tert*-butyl chloride, and isobutene as the proelectrophile. A salient characteristic of *tert*-butylation is the marked temperature dependence of the products composition (e.g., the meta/para ratio in the alkylation of toluene), a feature essential to our approach in that it provides a kind of thermometer to estimate the temperature of the intermediate INC2. In those cases where the INC1 → INC2 conversion is exothermic, which can be ensured by an appropriate choice of the ArH/P pair, there is a sudden release of energy, stored in INC2 exactly at the moment of its formation. Assuming that the excess internal energy is partitioned between the components of the complex before its conversion into the products, as expected for a process characterized by a sizable activation energy,[23] one can regard INC2 as an isolated system whose temperature is suddenly raised (chemical activation) to T_0, higher than the bath gas temperature, T. The fate of the "hot" INC2 depends on the competition among several processes. In principle, they could undergo dissociation, but the process is expected to be largely suppressed in gases at or above atmospheric pressure, a view fully supported by the trends emerging from mass spectrometric experiments specifically aimed at clarifying this relevant point (vide infra). The INC2 are therefore bound to evolve into the products, either via a "prompt" reaction at T_0, or via a thermal reaction at T, following collisional thermalization according to the scheme



where k^* and k are the unimolecular rate constants for alkylation at T_0 and T respectively, k_d is the bimolecular rate constant for collisional deactivation, and m^*/p^* and m/p are the meta/para ratios at T_0 and T, respectively. Since *tert*-butylation of toluene takes place only at meta and para positions, one can take $k^* = k^*_m + k^*_p$ and $k = k_m + k_p$.

Two limiting conditions can be envisaged where the observed meta/para ratio is independent of the nature and the pressure of the bath gas, namely, when $k^* \gg k_d[M]$, or $k^* \ll k_d[M]$. Between these extremes, the observed meta/para ratio is expected to change with the nature of the bath gas, which affects k_d, and with its pressure, to which $[M]$ is proportional. In principle, from a quantitative study of the isomeric composition of the products as a function of both parameters, one can estimate the rate constant of the prompt alkylation relative to the rate of collisional deactivation. Since the latter can be calculated with reasonable accuracy using the current theories on ion−molecule collisions, one is eventually in the position to estimate the lifetime of INC2, namely the time interval between its formation and conversion into the products.

The Alkylation Sequence. In the radiolytic experiments gaseous arenium ions were obtained from different reactions, depending on the nature of the bath gas. In the alkanes used, labeled toluenium ions are formed by proton transfer from the major ions, namely $C_nH_5^+$ ($n = 1,2$) and i-$C_3H_7^+$ produced upon irradiation of methane and propane, respectively.[15] The arenium

$$CD_3C_6D_5 + AH^+ \rightarrow A + CD_3C_6HD_5^+ \quad (3)$$
$$(A = CH_4, C_2H_4, C_3H_6)$$

ions, excited by the large exothermicity (Table 1) of reactions in eq 3, are likely to undergo intraannular H/D scrambling[33]

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(16) Aschi, M.; Attinà, M.; Cacace, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1589.

(17) Aschi, M.; Attinà, M.; Cacace, F. *J. Am. Chem. Soc.* **1995**, *119*, 12832.

(18) Aschi, M.; Attinà, M.; Cacace, F. *Res. Chem. Int.* **1996**, *22*, 645.

(19) Aschi, M.; Troiani, A.; Cacace, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *109*, 116.

(20) Cacace, F.; Giacomello, P. *J. Am. Chem. Soc.* **1973**, *95*, 5851.

(21) Sen Sharma, D. K.; Ikuta, S.; Kebarle, P. *Can. J. Chem.* **1982**, *60*, 2325.

(22) Giacomello, P.; Cacace, F. *J. Am. Chem. Soc.* **1976**, *98*, 1823.

(23) Cacace, F.; Ciranni, G. *J. Am. Chem. Soc.* **1986**, *108*, 887.

(24) Cacace, F.; Ciranni, G.; Giacomello, P. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1373.

(25) Cacace, F.; Crestoni, M. E.; de Petris, G.; Fornarini, S. *Can. J. Chem.* **1988**, *66*, 3099.

(26) Stone, J. M.; Stone, J. A. *Int. J. Mass Spectrom. Ion Proc.* **1991**, *109*, 247.

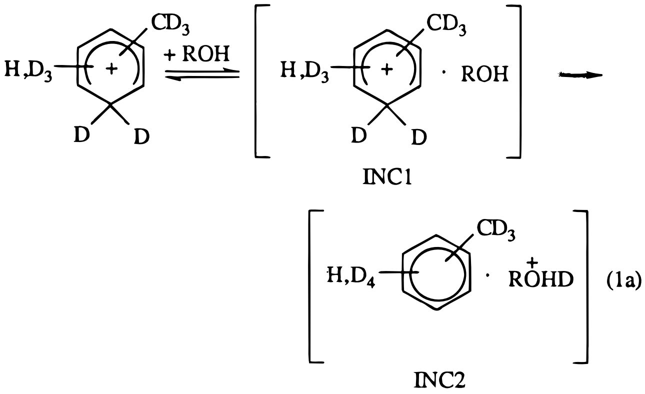
(27) Cacace, F.; Crestoni, M. E.; Fornarini, S. *J. Am. Chem. Soc.* **1992**, *114*, 6776.

(28) Cacace, F.; Crestoni, M. E.; Fornarini, S.; Kuck, D. *J. Am. Chem. Soc.* **1993**, *115*, 1024.

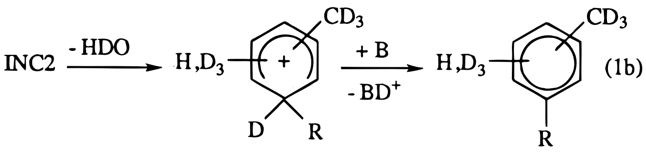
(29) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1989**, *17* (Suppl. No. 1).

(30) Szulejko, J. E.; McMahon, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 7839.

before being thermalized by a large number of collisions with the molecules of the bath gas and subsequently interacting with the proelectrophile (e.g., *tert*-butyl alcohol (ROH)) present at a low concentration in the system. Alkylation occurs following the general pattern of Crafts−Friedel reactions, according to the scheme

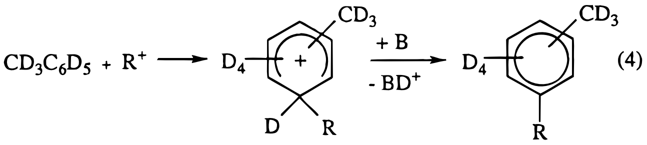


(1a)



(1b)

The use of deuterated toluene is necessary to discriminate between the intracomplex alkylation of interest and the conventional direct alkylation promoted by *tert*-butylating cations, such as R^+ and ROH_2^+, formed upon interaction of the gaseous Brønsted acids AH^+ with the proelectrophile. In fact, only the products from the sequence in eqs 1a,1b contain one H atom in the ring, whereas those from the direct alkylation contain a fully deuterated ring



(4)

An alternative route to toluenium ions was utilized, namely, methylation of benzene by dimethylfluoronium ions obtained from the irradiation of gaseous methyl fluoride (eq 5).[15] No

$$C_6H_6 + (CH_3)_2F^+ \rightarrow CH_3C_6H_6{}^+ + CH_3F \qquad (5)$$

labeled reagents are required in this case, since no toluene is present in the gaseous system, which prevents formation of *tert*-butyltoluenes by direct alkylation. To ensure fast deprotonation of the *tert*-butylated arenium ions, a strong gaseous base, $(C_2H_5)_3N$, was present at pressures up to 3 Torr in all irradiated systems. In this way, secondary isomerization of the alkylated arenium ions is suppressed,[23] at the expense, however, of the absolute yields, since the base intercepts a considerable fraction of the charged precursors.[15,17]

Table 1. Relevant Thermochemical Data

reaction	$\Delta H°$
$CH_5{}^+ + C_7H_8 \rightarrow CH_4 + CH_3C_6H_6{}^+$	$-58.2;^{a,b}$ $-57.5^{a,c}$
$C_2H_5{}^+ + C_7H_8 \rightarrow C_2H_4 + CH_3C_6H_6{}^+$	$-27.2;^{a,b}$ $-25.1^{a,c}$
$i\text{-}C_3H_7{}^+ + C_7H_8 \rightarrow C_3H_6{}^+ CH_3C_6H_6{}^+$	$-10.3;^{a,b}$ $-9.3^{a,c}$
$(CH_3)_2F^+ + C_6H_6 \rightarrow CH_3F + CH_3C_6H_6{}^+$	$-43.0;^{a,b}$ $-40.5^{a,c,d}$
$CH_3C_6H_6{}^+ + t\text{-}C_4H_9OH \rightarrow C_7H_8 + t\text{-}C_4H_9OH_2{}^+$	$-4.0^{a,b}$
$CH_3C_6H_6{}^+ + t\text{-}C_4H_9OH \rightarrow C_7H_8 + t\text{-}C_4H_9{}^+ + H_2O$	$+9.0^{a,b}$
$CH_3C_6H_6{}^+ + t\text{-}C_4H_9OH \rightarrow CH_3C_6H_5\text{-}t\text{-}C_4H_9{}^+ + H_2O$	$-11.3^{b,e}$
$CH_3C_6H_6{}^+ + t\text{-}C_4H_9Cl \rightarrow C_7H_8 + t\text{-}C_4H_9{}^+ + HCl$	$+13.5^{a,c}$
$CH_3C_6H_6{}^+ + t\text{-}C_4H_9Cl \rightarrow CH_3C_6H_5\text{-}t\text{-}C_4H_9{}^+ + HCl$	$-6.8^{a,c,e}$
$CH_3C_6H_6{}^+ + i\text{-}C_4H_8 \rightarrow C_7H_8 + t\text{-}C_4H_9{}^+$	$-6.1;^{a,b}$ $-4.0^{a,c}$
$CH_3C_6H_6{}^+ + i\text{-}C_4H_8 \rightarrow CH_3C_6H_5\text{-}t\text{-}C_4H_9{}^+$	$-24.3^{b,e}$

[a] Referred to the most stable isomer. [b] Reference 29. [c] Reference 30. [d] From the heat of formation of $(CH_3)_2F^+$ (refs 31 and 32). [e] Referred to the formation of *p-tert*-butyltoluene, whose PA is taken equal to that of *tert*-butylbenzene.

Results

Mass Spectrometric Experiments. The specific purpose of these experiments was the evaluation of the rate of INC2 dissociation relative to that of alkylation as a function of the pressure. In the FT-ICR experiments, toluenium ions produced in the external CI source from the reaction in eq 3 were isolated by selective-ejection techniques and allowed to react at 25 °C in the resonance cell with the proelectrophile RX ($R = t\text{-}C_4H_9$, $X = OH$, Cl) at pressures ranging from 10^{-8} to 10^{-7} Torr. Toluenium ions were found unreactive toward RCl, whereas they underwent efficient proton transfer to ROH yielding ROH_2^+, namely, the product expected from INC2 dissociation, with a collisional efficiency of ca. 70% based on the collision rate constant k_c calculated utilizing the ADO theory[34] or the Su and Chesnavich trajectory algorithm,[35] which in this case give very close results. Formation of $RC_7H_8^+$ alkylated adducts was barely detectable, its collisional efficiency being of the order of 1%. Clearly, in the pressure domain accessible to FT-ICR mass spectrometry dissociation predominates over alkylation.

These observations are hardy surprisingly since the lack of collisional stabilization typical of the FT-ICR experiments causes the considerable electrostatic energy released by the association of the arenium ion with the proelectrophile to remain stored in INC1 and hence in the daughter INC2, which contains a large excess of internal energy, namely, that already present in INC1 plus the (smaller) contribution from INC1 → INC2 conversion. Such hot INC2 can be expected to be extremely short-lived, which then prevents observation, and to undergo entropically favored processes, such as the observed dissociation into their components.

In the TQMS experiments, toluenium ion from the reaction in eq 3 were selected with the first quadrupole and allowed to react at 25 °C with the RX proelectrophile contained in the hexapolar cell at pressures ranging from 1.5×10^{-6} to 5.0×10^{-5} Torr. The ions formed, analyzed with the third quadrupole, belong to two different classes: (i) the alkylated adduct $RC_7H_8^+$ and the product from its further reaction with RX, namely the $R_2C_7H_7^+$ dialkylated adduct; (ii) ions taken as indicative of INC2 dissociation, whose nature depends on the specific proelectrophile employed. For RCl, we observed R^+ and $R^\bullet C_4H_8^+$, the product from its further reaction with RCl. For ROH, R^+ and ROH_2^+ were accompanied by the products from their further reactions with ROH, namely, $(ROH)_2H^+$, R_2OH^+ and $R^\bullet C_4H_8^+$. The plots of the relative intensity of ions of class i- vs the pressure, reported in Figures 1 and Figure 2 for the reactions

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(31) McMahon, T. B.; Heinis, T.; Nicol, G.; Horvey, J. K.; Kebarle, P. *J. Am. Chem. Soc.* **1988**, *110*, 7591.

(32) The data of ref 31 have been adjusted to the scale revised by the following: Glukhovtsev, M. N.; Szulejko, J. E.; McMahon, T. B.; Gauld, J. W.; Scott, A. P.; Smith, B. J.; Pross, A.; Radom, L. *J. Phys. Chem.* **1994**, *98*, 13099.

(33) Intraannular 1,2 H shifts are characterized by a relatively low barrier (e.g., 7.6 ± 0.2 kcal mol^{-1}) in gaseous *tert*-butyltoluenium ions, see: ref 27.

(34) Bowers, M. T.; Su, T. *Interactions between Ions and Molecules*, Ausloos, P., Ed; Plenum Press: New York 1975; p 163.

(35) Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183.

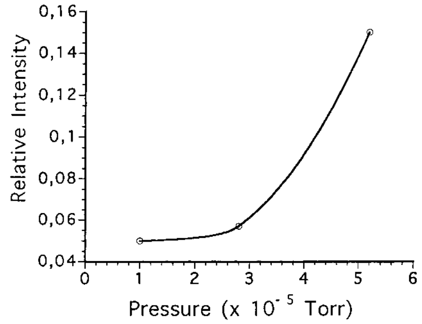

Figure 1. Pressure dependence of the relative efficiency of alkylation of toluenium ions by ROH (R = t-C_4H_9) expressed as the ratio of the combined intensities of the $RC_7H_8^+$ and $R_2C_7H_7^+$ ions to the total intensity.

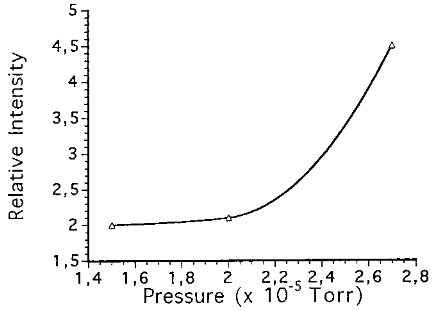

Figure 2. Pressure dependence of the relative efficiency of the alkylation of toluenium ions by RCl (R = t-C_4H_9), expressed as in Figure 1.

of $C_7H_9^+$ with ROH and RCl, respectively, at a (nominal) center-of-mass energy of 0.15 eV, show a dramatic increase of the alkylation efficiency with the pressure, obviously at the expense of the dissociation channel.

The mass spectrometric results speak against a kinetically significant role of the dissociation channel in the radiolytic experiments. This conclusion rests on the extrapolation to much higher pressures of the trend emerging from the FT-ICR and the TQMS experiments, showing that the rate of alkylation, negligible at 10^{-8}−10^{-7} Torr, becomes comparable to that of dissociation even at pressures as low as 10^{-4} Torr. Furthermore, the TQMS experiments provide only a *lower limit* of the alkylation/dissociation branching ratio, in that the $C_7H_9^+$ ions utilized as the charged reagent have excess translational energy, as required for their extraction from the ion source and injection into the second quadrupole. As expected, and confirmed by control experiments performed by changing the kinetic energy of the $C_7H_9^+$ ions, the relative efficiency of the dissociation channel undergoes a steep decline as the energy is decreased and can be expected to be quite low in the radiolytic experiments, where the ions have a thermal energy distribution.

Table 2. Positional Selectivity of Intracomplex *tert*-Butylation of Toluenium Ions by Different Proelectrophiles

T (°C)	bath gas (Torr)[a]	proelectrophile	meta/para ratio
25	CH_4 (50)	t-C_4H_9OH	0.408 ± 0.005
25	CH_4 (150)	t-C_4H_9OH	0.316 ± 0.004
25	CH_4 (760)	t-C_4H_9OH	0.163 ± 0.003
25	CH_4 (6 atm)	t-C_4H_9OH	0.053 ± 0.003
25	CH_4 (50)	t-C_4H_9Cl	0.266 ± 0.005
25	CH_4 (150)	t-C_4H_9Cl	0.219 ± 0.005
25	CH_4 (760)	t-C_4H_9Cl	0.163 ± 0.004
25	CH_3F (50)[b]	i-C_4H_8	0.428 ± 0.005
25	CH_3F (150)[b]	i-C_4H_8	0.299 ± 0.005
25	CH_3F (760)[b]	i-C_4H_8	0.149 ± 0.005
25	C_3H_8 (50)	t-C_4H_9OH	0.149 ± 0.005
25	C_3H_8 (150)	t-C_4H_9OH	0.111 ± 0.003
25	C_3H_8 (300)	t-C_4H_9OH	0.080 ± 0.006
25	C_3H_8 (760)	t-C_4H_9OH	0.053 ± 0.004
25	C_3H_8 (3.50 atm)	t-C_4H_9OH	0.052 ± 0.06
25	C_3H_8 (50)	t-C_4H_9Cl	0.124 ± 0.004
25	C_3H_8 (150)	t-C_4H_9Cl	0.111 ± 0.005
25	C_3H_8 (300)	t-C_4H_9Cl	0.095 ± 0.006
0	C_3H_8 (760)	t-C_4H_9Cl	0.075 ± 0.005
0	C_3H_8 (760)	t-C_4H_9OH	0.042 ± 0.001
42	C_3H_8 (760)	t-C_4H_9Cl	0.064 ± 0.002
42	C_3H_8 (760)	t-C_4H_9OH	0.053 ± 0.005
0	C_3H_8 (760)	t-C_4H_9Cl	0.064 ± 0.001
25	CH_3F (760)[b]	i-C_4H_8	0.111 ± 0.002
25	CH_4 (50)	t-C_4H_9OH	0.408 ± 0.005

[a] All systems contained O_2 (10 Torr) as a radical scavenger, $CD_3C_6D_5$ (3 Torr), the proelectrophile (3 Torr), and $(C_2H_5)_3N$ (3 Torr). [b] These systems contained C_6H_6 (3 Torr) instead of C_7D_8.

Radiolytic Experiments. The alkylation of toluene was investigated in different bath gases: CH_4, C_3H_8, and CH_3F at temperatures ranging from 0 to 42 °C at pressures from 50 to 4560 Torr. In addition to those of *tert*-butyltoluenes, the ionic reactions occurring in the gaseous system gave a variety of products from direct alkylation processes (e.g., isomeric ethyltoluenes in CH_4, isomeric cymenes in C_3H_8, etc.), consistent with earlier results.[15] In view of the specific purpose of this work, attention was focused on those *tert*-butyltoluenes that, according to the criteria outlined in a previous section, are formed via the sequence in eq 1. Their yields, of the order of 10^{-3} molecules per 100 eV, are relatively low, as a consequence of the addition to the irradiated gas of the base, $(C_2H_5)_3N$, which intercepts a large fraction of the charged precursors (i.e., $C_nH_5^+$ in CH_4, i-$C_3H_7^+$ in C_3H_8, and $(CH_3)_2F^+$ in CH_3F, as well as the toluenium ions). Only *m*- and *p*-*tert*-butyltoluene are formed, whose ratios are reported in Table 2. Two features of the results are salient. First, in the pressure range investigated, the isomeric composition of the products, expressed by their meta/para ratio, actually displays a strong pressure dependence, suggesting that prompt alkylation and collisional cooling of hot INC2 occur at a comparable rate, which represents a necessary condition for the application of the chemical activation approach. Second, the three bath gases display a different deactivating power, C_3H_8 being significantly more effective than CH_4 and CH_3F. Thus, the alkylation promoted by *tert*-butyl alcohol displays the *highest* positional selectivity, suggestive of the *lowest* reaction temperature and reflected by a meta/para ratio as low as 0.05, in C_3H_8 at 760 Torr. The same selectivity, and hence the same meta/para ratio, is observed in CH_4 at a pressure of 4560 Torr and similar trends prevail in the reactions involving *tert*-butyl chloride and isobutene. Such findings are accounted for by the larger k_d of C_3H_8 than of CH_4 and CH_3F in the process in eq 2b. In fact, one can take $k_d = \beta_c k_c$, where k_c is the collision rate constant which, according to current theories,[34,35] is comparable for all the bath gases employed, and β_c is the efficiency for the collisional removal of a sufficiently large fraction of excess internal energy from hot INC2* as to make prompt alkylation a slow process in comparison with further collisional cooling. It follows that the higher k_d of C_3H_8 is to be traced to a higher β_c value, reflecting the larger number and the better frequency matching of its vibrational and internal rotations modes with those of the hot INC2. The higher β_c of C_3H_8 is not unexpected, based on trends firmly established from kinetic studies of unimolecular reactions of neutral[36] and ionic species.[37] Additional radiolytic experiments were performed, aimed at evaluating the temperature dependence of the meta/

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(36) Robinson, P. J.; Holbrock, K. A. *Unimolecular Reactions*; Wiley: New York, 1972; Chapter 10 and references therein.

(37) Ahmed, M. S.; Dunbar, R. C. *J. Am. Chem. Soc.* **1987**, *109*, 3215 and references therein.

Table 3. Rate Constants Ratios for “Prompt” and Thermal Alkylation[a]

reaction	bath gas[b]	k^*_m/k^*_p [c]	k_m/k_p [c]
$CD_3C_6HD_5^+ + t\text{-}C_4H_9OH$	CH_4	0.4	0.04
$CD_3C_6HD_5^+ + t\text{-}C_4H_9OH$	C_3H_8	0.4	0.04
$CD_3C_6HD_5^+ + t\text{-}C_4H_9Cl$	CH_4	0.2	0.07
$CD_3C_6HD_5^+ + t\text{-}C_4H_9Cl$	C_3H_8	0.2	0.05

[a] From the best fitting plots, see text. [b] Bath gas temperature 25 °C. [c] Standard deviation of the ratios. ±10%.

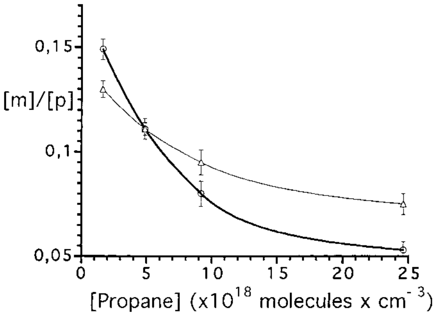

Figure 3. Best fit with eq 6 of the experimental data for the alkylation of toluenium ions by ROH (○) and RCl (△) in propane at 298 K.

para ratio in C_3H_8 at 760 Torr, using both *tert*-butyl alcohol and *tert*-butyl chloride as the proelectrophiles. Regression analysis of the linear (correlation coefficients from 0.970 to 0.999) Arrhenius plots from experiments performed at 0, 25, and 42 °C gave phenomenological $E°_m - E°_p$ activation energies differences of 1.8 ± 0.4 and 1.4 ± 0.4 kcal mol^{-1} for the alkylation of toluenium ions by *tert*-butyl alcohol and *tert*-butyl chloride, respectively.

Discussion

Application of the steady-state approximation to the competing reactions in eqs 2a and 2b yields the following expression for the observed meta/para ratio as a function of the number density, [*M*], of the bath gas molecules

$$\left(\frac{\text{meta}}{\text{para}}\right)_{\text{obsd}} = \frac{(k_m + k_p)k^*_m + k_d\,[M]\,k_m}{(k_m + k_p)k^*_p + k_d\,[M]\,k_p} \qquad (6)$$

Accordingly, the meta/para ratio observed at the low-pressure limit is that typical of the prompt reaction at T_0, corresponding to the k^*_m/k^*_p ratio, whereas at the high-pressure limit, the observed meta/para ratio is that typical of the thermal alkylation at *T*, corresponding to k_m/k_p. Between these extremes, the observed ratio reflects a combination of k^*_m/k^*_p and k_m/k_p ratios, whose relative weight depends on the relative rate of the prompt alkylation and the collisional deactivation at the pressure of the experiment. The numerical fitting of the data with the trend predicted by eq 6 is good for all systems investigated (correlation coefficient greater than 0.99), which allows evaluation of the k^*_m/k^*_p and k_m/k_p ratios reported in Table 3.

The Strong Collision Approximation. We apply now, limited to the reactions occurring in propane (see Figure 3), the strong-collision approximation, assuming that the first collision with the deactivating molecule is sufficient to decrease the temperature of the hot INC2 to such an extent as to upset the balance between the rate of the prompt alkylation and that of collisional deactivation in favor of the latter. In other words, unless hot INC2 react *before* the first deactivating collision, they are bound to undergo thermalization which amounts to take $\beta_c = 1$. Such an assumption, frequently adopted in the kinetic study of thermal and photochemical reactions between neutral species, does not seem unrealistic in the case of interest, if one considers that the rate of reaction and of collisional deactivation of hot INC2 are of the same order of magnitude even in CH_4 and CH_3F, as shown by the strong pressure-dependence of the isomeric composition of the products, and that $\langle \Delta E \rangle$, the average energy transferred per collision, is expected to be significantly larger for C_3H_8 than for CH_4 or CH_3F. In this connection, it is most significant that the observed meta/para ratio does not undergo any further change on raising the pressure of the C_3H_8 bath gas from 1.0 to 3.5 atm, indicating that the limit of strong-collision stabilization is reached, or very closely approached, in C_3H_8 at 760 Torr.[38]

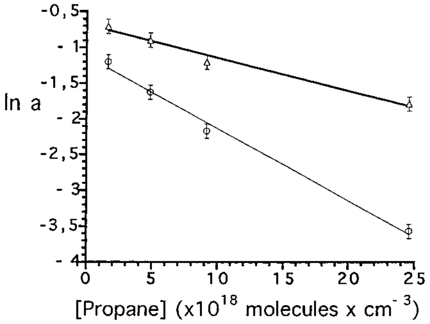

Figure 4. Logarithmic plot of *a*, the fraction of INC2 that react before colliding with the bath gas molecules as a function of their number density [*M*] for the reactions promoted by ROH (○) and RCl (△).

Evaluation of the Lifetime of INC2. According to the strong-collision model, the products are formed either from the prompt reaction at T_0, or from the thermal reaction at the temperature T of the bath gas, without significance contributions from reactions occurring in complexes at intermediate temperatures. Denoting with *a* the fraction of products from hot INC2, one obtains

$$\left(\frac{\text{meta}}{\text{para}}\right)_{\text{obsd}} = a\frac{m^*}{p^*} + (1 - a)\frac{m}{p} = a\frac{k_m}{k_p} \qquad (7)$$

which allows calculation of *a* from the data of Table 3. In this framework, *a* is the fraction of hot INC2 *which experience no collisions* during their lifetime *t* (i.e., before conversion into the products) and hence is given by

$$a = \exp(-\beta_c k_c [M] t) \qquad (8)$$

The linear dependence of ln *a* on [*M*] is verified by the plots illustrated in Figure 4 , both characterized by a correlation coefficient of 0.996. From the slope, $\beta_c k_c t$, one can derive the mean lifetime of the hot INC2 utilizing the ion−molecule collision rate constant k_c provided by current theories[34,35] and taking $\beta_c = 1$, as discussed above. In turn, since $t = 1/k^* = 1/(k^*_m + k^*_p)$, one can calculate the values of k^*_m and k^*_p (Table 4).

Two sources of errors need to be considered in evaluating these results, in particular as concerns the lifetime of INC2*. The contributions from the experimental errors of the input data and from the best-fit procedures are not unduly large, introducing a cumulative uncertainty conservatively estimated below 20%. Probably larger, and certainly more difficult to estimate, is the uncertainty attached to the collision rate constant k_c, utilized as the anchor to calculate the rate constants for alkylation

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(38) The experiments in C_3H_8 at 3.50 atm were performed in compliance with the comment of one of the reviewers, who pointed to the need to unambiguously show that the strong-collision stabilization limit is indeed reached in C_3H_8 at 1 atm.

Table 4. Approximate Lower Limits for the Lifetime of INC2* and Rate Constants for Intracomplex Alkylation Derived Assuming These Lifetimes[a]

proelectrophile (P)	mean lifetime (s)	k^*_m (s^{-1})	k^*_p (s^{-1})
t-C_4H_9OH	1×10^{-10}	3×10^9	7×10^9
t-C_4H_9Cl	5×10^{-11}	3.3×10^9	1.7×10^{10}

[a] For a discussion of the estimated uncertainty range, see text.

and, hence, the INC2* lifetime. The k_c value was obtained from the ADO theory[34] and the trajectory algorithm,[35] which lead in this case to practically identical results.[39] In the vast majority of cases where comparison is possible, the collision rate constants from both methods, in particular from the Su and Chesnavich algorithm,[35] fall within ±30% of the experimental values.[40] Assuming the same range in the case of interest, one arrives to a cumulative uncertainty of ±40% for the lifetime of *hot* INC2* given in Table 4.

The above analysis presupposes the validity of the model adopted, which embodies a simplified kinetic scheme, and especially of the strong collision approximation, currently adopted in recent kinetic studies of ion−molecule reactions.[41] Of particular interest to the present discussion are the results of a very recent R2PI−HPMS study[42] that characterize C_3H_8 as an efficient third body, with a collisional efficiency near unity, in the stabilization of excited $[CH_3C_6H_5(C_4H_8)]^+$ INC, remarkably similar, and formed from a reaction remarkably similar, to those studied in this work. Nevertheless, in the lack of positive evidence for the quantitative validity of the strong collision hypothesis in the systems of interest, it is legitimate to assess the uncertainty range associated to a significant departure of the collisional efficiency β_c from the assumed unity value. Whereas a value as low as 0.1 is conceivable, which would lead to INC2* lifetimes up to 1 ns, a conservative analysis of the various uncertainty sources and the adoption of a more realistic lower limit for the β_c of C_3H_8 suggest that the INC2* lifetimes should not exceed a few tenths of a nanosecond.

As a final matter of interest, the temperature of hot INC2 can roughly be estimated from the k^*_m/k^*_p ratio (Table 3) and the Arrhenius parameters of the alkylation provided by the temperature-dependence study reported in the previous section. The results show that the temperature increase caused by the INC1 → INC2 conversion is of the order of 450 and 250 K in the case of t-C_4H_9OH and t-C_4H_9Cl, respectively, with an uncertainty of ±150 K. From the estimated temperatures, and utilizing the equation of Klots,[43] one can, in principle, evaluate the well depth of the gaseous complexes of interest. We feel, however, that owing to the rough approximations involved in the temperature estimates and the unavoidable propagation of errors, the results would be affected by intolerably large uncertainties.

Conclusions

The chemical activation approach outlined in this paper has allowed approximate evaluation of the lifetime of genuine INC, previously identified as the charged intermediates in the gas-phase Crafts−Friedel alkylation. Whereas the approach is experimentally laborious and the results approximate, nevertheless to our knowledge, they represent the first experimental data on the lifetime of such ion−neutral complexes. Depending on their nature, the species investigated have mean lifetimes in the range up to a few tenths of a nanosecond that seem appropriate for gaseous INC which, by definition, must satisfy the Longevialle criterion,[8] namely, be sufficiently long-lived to allow mutual rotation on their components.

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(39) Such an agreement is rather common, see: Jarvis, G. K.; Mayhew, C. A.; Tuckett, R. P. *J. Phys. Chem.* **1996**, *100*, 17166.

(40) However, see: Dougherty, R. C.; Xu, M. *J. Am. Chem. Soc.* **1996**, *118*, 9424.

(41) For instance, see: (a) Li, C.; Ross, P.; Szuleiko, J. E.; McMahon, T. B. *J. Am. Chem. Soc*. **1996**, *118*, 9360. (b) Sahlstrom, K. E.; Knighton, W. B.; Grimsrud, K. P. *J. Phys. Chem.* **1997**, *101*, 5543. These authors utilize the strong collision approximation and discuss as well the conceivable range of β_c of CH_4 in the stabilization of $[CH_3BrCl^-]$ complexes, estimating a upper limit of 7 ps based on the comprehensive study reported in ref 37. According to the general correlation given in the latter study, C_3H_8 is approximately 3.4 times more efficient than CH_4 in our systems.

(42) Meot-Ner (Mautner), M.; Pithawalla, Y. B.; Gao, J.; El-Shall, M. S. *J. Am. Chem. Soc.* **1997**, *119*, 8332.

(43) Klots, C. E. *J. Phys. Chem.* **1992**, *96*, 1733 and references therein.