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Catalysed quaternization of coordinated tertiary amines by ethyl iodide: kinetics and mechanism

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Abstract

A kinetic study of the joint homogeneous–heterogeneous catalysis for the quaternization of silver (I)-coordinated triethylamine and tributilamine by ethyl iodide was performed in toluene. The data obtained substantiated the superficial molecular arrangement, previously proposed by Barbosa and Spiro, and exposed a new competitive reaction of the non-coordinated soluble silver salt with the alkyl halide in the solvent under study. Estimates of the solution rate constants were obtained for both systems and evidence of a surface effect is also presented. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Kinetics; Catalysed quaternization; Coordinated amines; Superficial molecular arrangement

1. Introduction

Structural and mechanistic similarities of catalytic pathways in homogeneous, heterogeneous and enzymatic systems became clearer over the last decades, with the development of new and powerful instrumentation techniques and lead to a progressive tendency for structural and mechanistic studies at the molecular level in catalysis [1]. In particular, over the last two decades, the significant contribution of Yermakov et al. in the intentional synthesis of active sites on heterogeneous catalysts must be referenced. This remarkable contribution, resorting to the attachment of metal complexes to support surfaces, involved a molecular tailoring construction process over catalytic supports [1,2]. Several synergistic effects reported in the literature [3–6] frequently called up to the same type of interpretations. Synergistic effects on the heterogeneous catalysis of organic halide solvation reactions by insoluble silver and mercury salts [3,4], as well as joint homogeneous–heterogeneous catalysis for triethylamine quaternization in an aromatic solvent [5,6], have been reported and interpreted at a molecular level. For unimolecular solvation reactions, the interpretation was based on the assisted cleavage of the carbon–halogen bond by Ag^{+} and Hg^{2+} surface sites [3,4], while the catalysis of the bimolecular quaternization of silver-coordinated triethylamine by ethyl iodide in benzene was attributed to a favourable surface arrangement of the reacting molecules [5].

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In this work, a kinetic study of the joint homogeneous–heterogeneous catalytic effect of silver salts on the quaternization of tertiary amines by ethyl iodide was undertaken aiming at a deeper understanding of this complex reaction system.

The hypothesis of a bimolecular homogeneous–heterogeneous reaction [5] between the coordinated amine and ethyl iodide was considered initially, however, a data analysis of the experimental data obtained, monitoring the amine concentration in solution, showed the inadequacy of the fits to the corresponding rate equations. The type of response observed under various experimental conditions prompted a reanalysis of the overall reaction system in search of any underlying incorrect assumptions and lead to the hypothesis of a competitive side reaction. This possibility was considered and tested, monitoring simultaneously the reaction media in terms of the total amine and silver concentration.

A preliminary kinetic analysis of this intricate reaction system was undertaken and the rate equations deduced were tested with the data obtained for two amines (Et_3N and Bu_3N). The quality of the data fit registered in these runs clearly showed the validity of the hypothesis put forward apart from allowing the calculation of guess estimates for the solution rate constants of the coordinated tertiary amines quaternization also evidenced the surface effect of silver iodide on the quaternization reactions.

2. Experimental

2.1. Reagents and solutions

Toluene (Aristar grade; purity $\geq 99.95\%$) was supplied by BDH and was used without further purification.

The amines, triethylamine (Merck — p. synthesis) and tributilamine (BDH — GPR), were treated with acetic anhydride and fractionally distilled, then refluxed over potassium hydroxide and finally fractionally distilled from barium oxide through a column packed with Pyrex glass rings, as described by Barbosa and Lampreia [7]. Tributilamine was distilled under a reduced pressure of 1 kPa.

Ethyl iodide (BDH — GPR grade; purity $\geq 99\%$) showed the yellowish colour characteristic of its photochemical decomposition [8]. Successive washings with dilute sodium thiosulphate solutions removed the free iodine. The final solution was dried with anhydrous calcium chloride and finally fractionally distilled over sodium wire [8].

The purity of all liquids was determined by GC, being 99.98% for the solvent toluene, 99.94% for triethylamine, 99.98% for tributilamine and 99.75% for ethyl iodide.

Silver nitrate (GPR grade; purity $\geq 99.8\%$) was supplied by BDH and was used without further purification.

Silver iodide was synthesised by a slow addition of equal volumes of potassium iodide silver nitrate solutions ($\cong 0.20$ M), under constant stirring. The precipitate was separated by decantation and thoroughly washed with doubly distilled water. The solid was dried, for 12 to 14 h at 378 K, under reduced pressure: $P < 100$ Pa [9,10], and finally ground and sieved (≤ 210 μm) in order to collect freshly prepared samples to use in the kinetic runs. X-ray diffraction and BET specific surface area determinations were used to characterise silver iodide samples from independent preparations and showed that the solid was polycrystalline, predominantly composed of β-AgI and had a BET (N_2) specific surface area of 0.407 ± 0.003 $m^2 g^{-1}$.

Solutions of the tertiary amines and ethyl iodide in toluene were prepared by weight in volumetric flasks. The liquids were added under a light N_2 flux over the neck of the flask to minimise the competitive amine auto-oxidation reaction [11], which accompanies the silver–amine coordination [6].

2.2. Kinetic runs

The kinetic experiments were performed in round-bottom glass vessels, immersed in a thermostatic bath and under constant stirring. The bath temperature, which was kept at 25.0 ± 0.05°C with a Braun Thermomix UB thermostat immersed in an isolated water bath and stirring at 2500 rpm, was guaranteed by MAGIMM immersible magnetic stirrers from Rank brothers.

The reaction mixtures were prepared dissolving different weighed quantities of solid silver nitrate in solutions of amine in toluene prior to the introduction of silver iodide.

The solid, previously weighed, was added through a funnel with a ground glass joint, fitting the reaction flask, in order to avoid any losses in the vessel's neck during transfer. Finally, after a thermostatic pre-stabilisation of at least 30 min, the appropriate amount of ethyl iodide solution in toluene was added.

The kinetic runs were monitored, collecting reaction mixture samples rapidly, with automatic pippeting devices from Gilson and under continuous stirring to minimise changes in the solution–solid ratio [4]. The amine content was determined by potentiometric back titration, a procedure that proved itself convenient as the reaction under study is stopped simultaneously.

2.2.1. Amine titration

Acid–base titration, in anhydrous acetic acid, is the usual procedure to determine the amine concentration, but this analysis is subject to the interference of metallic acetates [12,13]. Furthermore, unsuspected interference in standard analytical methods due to side catalytic reactions have been reported [14,15]. Under these circumstances, preliminary tests with synthetic reaction mixtures are absolutely necessary to evaluate any method under specific experimental conditions. The data for the analysis of synthetic reaction mixture samples, presented in Table 1, showed that solid silver iodide does not interfere, but silver ions lead to positive interference in the quantitative determination of amines.

According to J.W. Smith [16] a potentiometric break large enough to allow the detection of the end-point for titrations in aqueous media is obtained for all amines with $pK_a \geq 9$, therefore, quantitative determinations should be accurate for both amines under study as long as amine solubility is ensured. Bearing this in mind, amine solution samples were added to aqueous solutions of perchloric acid (≈ 0.01 M) and the excess acid back-titrated with sodium hydroxide (≈ 0.04 M) using an automatic titration assembly Radiometer RTS in the derivative mode. Water, freshly distilled under N_2 and over permanganate, was used in the preparation of all aqueous solutions and the sodium hydroxide solutions were stored in the polypropylene burette reservoir under soda lime and regularly standardised potentiometrically with potassium

Table 1
Tests on the anhydrous acetic acid acid–base titration of tertiary amine solutions containing soluble and insoluble silver salts

v_{HClO_4}/ml	v_{Sample}/ml	Composition/M	m_{AgI}/g	v_{eqv}/ml
5.0	–	–	–	11.85
5.0	1.0	Toluene	–	11.85
5.0	1.0	Toluene	0.02	11.84
5.0	1.0	EtI/0.040	–	11.84
5.0	1.0	EtI/0.040	0.02	11.85
10.0	1.0	Et_3N/0.040	–	16.18
10.0	1.0	Et_3N/0.040	0.02	16.17
10.0	1.0	Et_3N/0.040;$AgNO_3$/0.002[a]	–	15.79
10.0	1.0	Et_3N/0.040;$AgNO_3$/0.002[a]	0.02	15.78
10.0	1.0	Et_3N/0.040;$AgNO_3$/0.020[a]	–	12.41
10.0	1.0	Et_3N/0.040;$AgNO_3$/0.020[a]	0.02	12.40

$[HClO_4] = 1.259 \times 10^{-2}$ M and $[CH_3COONa] = 5.312 \times 10^{-3}$ M.

[a] A white precipitate is formed.

hydrogen phthalate. The potentiometric titration was monitored using a pH Meter Radiometer PHM64, a Radiometer G2040C glass electrode and a Radiometer K4040 reference calomel electrode. The titration of tributilamine titration was tested in the presence and absence of ethanol (added to increase the amine solubility), and it was concluded that in acid media, the results are identical within the burette uncertainty (± 0.001 ml).

The reliability of this analytical procedure to determine the amine content in the reaction system under study was also assessed using synthetic reaction mixtures of both amines once more. These tests, presented in Table 2, demonstrated that the titrations can be accurately performed in the presence of soluble and insoluble silver salts, as well as in the presence of tetralkylamonium salts.

Finally, additional tests were undertaken to ensure the reliability of the presence of an excess acid as a procedure to interrupt the amine quaternization. The results for these tests, involving crossed comparisons between back titrations of reaction mixtures made immediately after the addition of reaction mixture and after 5 or 15 min, proved to be identical within the experimental uncertainty and were also included in Table 2.

2.2.2. Reaction products

The solid reaction products for the quaternization reaction of triethylamine with ethyl

Table 2
Tests on the aqueous acid–base back titration of tertiary amine solutions in toluene, containing soluble and insoluble silver salts

v_{HClO_4}/ml	v_{Sample}/ml	Composition/M	$v_{C_2H_5OH}$/ml	m_{AgI}/g	m_{R_4NX}/g	v_{eqv}/ml
5.00	–	–	–	–	–	1.298
5.00	0.4	Et_3N/0.060	–	0.01	–	0.514
5.00	0.4	Et_3N/0.060	–	–	–	0.515
5.00	0.4	Et_3N/0.060;$AgNO_3$/0.040	–	0.01	–	0.515
5.00	0.4	Et_3N/0.060;$AgNO_3$/0.040	–	–	–	0.514
5.00	0.4	EtI/0.060	–	–	–	1.299
5.00	0.4	EtI/0.060	–	0.01	–	1.298
5.00	0.4	Bu_3N/0.058	–	–	–	0.541
5.00	0.4	Bu_3N/0.058	1.00	–	–	0.540
5.00	0.4	Bu_3N/0.058	1.00	0.01	–	0.542
5.00	0.4	Bu_3N/0.058;$AgNO_3$/0.032	1.00	0.01	–	0.541
5.00	0.4	Bu_3N/0.058;$AgNO_3$/0.032	–	–	–	0.541
5.00	0.4	Bu_3N/0.058;$AgNO_3$/0.032	–	0.01	0.002 (Bu_4NNO_3)	0.540
5.00	0.4	Bu_3N/0.058;BuI/0.060	–	0.01	–	0.541
5.00	0.4	Bu_3N/0.058;BuI/0.060	–	–	0.002 (Bu_4NI)	0.541
5.00	0.4 + 0.4	$Bu_3N/0.058; AgNO_3/0.032$ + $EtI/0.060$	–	0.01	–	0.541
5.00	0.4 + 0.4	$Bu_3N/0.058; AgNO_3/0.032$ + $EtI/0.060$	–	–	–	0.542
5.00	0.4 + 0.4	$Bu_3N/0.058; AgNO_3/0.032$ + $EtL/0.060$	–	–	–	0.541[a]
5.00	0.4 + 0.4	$Bu_3N/0.058; AgNO_3/0.032$ + $EtI/0.060$	–	–	–	0.542[b]

$[HClO_4] = 7.956 \times 10^{-3}$ M and $[NaOH] = 3.0647 \times 10^{-2}$ M.

[a] Titrated 5 min after the addition of an excess of $HClO_4$.

[b] Titrated 15 min after the addition of an excess of $HClO_4$.

iodine in toluene in the presence of soluble silver nitrate were analysed and confirmed the data of Barbosa and Spiro [5] for the same reaction system in benzene. The solid reaction products are composed of a water-soluble fraction and another insoluble. The soluble fraction contained a nitrate salt, detected using the $FeSO_4 \cdot NO$ spot test [17], which was identified as tetraethylamonium nitrate by elementary analysis data for carbon, hydrogen and nitrogen. The insoluble fraction was identified through solubility tests as silver iodide.

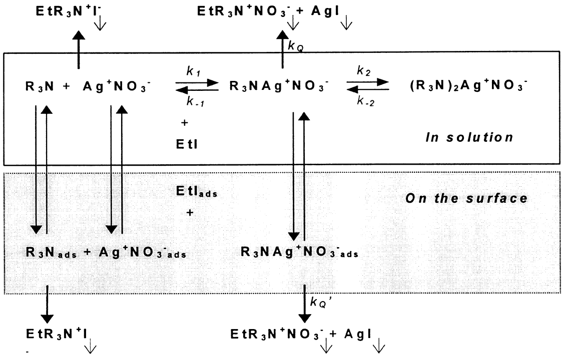
3. Results and discussion

A systematic study of the reaction

$$R_3N + R_3NAg^+NO_3^- + EtI \xrightarrow{AgI} R_4N^+NO^-_{3\downarrow} + AgI_\downarrow + R_4N^+I^-_\downarrow$$

in toluene was undertaken, bearing in mind the solution and surface contributions according to the preliminary Scheme 1. In this representation, k_Q and k'_Q are respectively the rate constants for the solution and surface catalysed quaternization of the coordinated amines by the ethyl iodide and $K_1 = k_1/k_{-1}$ and $K_2 = k_2/k_{-2}$ are the equilibrium constants for the formation of the 1:1 and 1:2 silver–amine complexes.

Experimental conditions adequate for the predominance of the amine in the form of a 1:1 silver complex, $R_3NAg^+NO_3^-$, prior to the beginning of the quaternization reaction, were chosen.



Scheme 1. Preliminary schematic representation of the molecular model proposed to interpret the synergistic effect of soluble and insoluble silver salts in the quaternization of tertiary amines by alkyl iodides in aromatic solvents.

Several kinetic runs with both amines and under different initial conditions were performed. The experimental data obtained in independent kinetic runs of reaction mixtures 0.04025 ± 0.0002 M triethylamine and 0.03994 ± 0.0005 M silver nitrate, initiated by the addition of ethyl iodide 0.03805 ± 0.0001 M, in the absence and in the presence of solid silver iodide, are presented in Table 3. These data are plotted in Fig. 1 and clearly show the surface effect on the quaternization rate.

In these experimental data sets, the initial rate of reaction, measured in terms of amine consumption, increased about 1000 times when compared with the corresponding rate in the absence of coordinated amine, $k_{Et_3N+EtI} = 3.3 \times 10^{-6}$ M^{-1} s^{-1} [18,19], $k_{Bu_3N+EtI} = 6.2 \times 10^{-7}$ M^{-1} s^{-1} [20], thus allowing the contributions of these reactions, for the overall kinetics, to be neglected hereon forward.

After a preliminary correction of the experimentally determined amine concentration due to the presence of solid in the collected reaction mixture sample, it is possible to calculate the concentration of the 1:1 silver–amine complex, $[R_3NAgNO_3]$, for every instant t. The volume of solid collected, v_s, was estimated considering that the amount of tetraalkylamonium iodide formed was negligible when compared with the corresponding tetraalkylamonium nitrate and silver iodide, Δn_i, formed in the same period. Accordingly, the volume of solid formed was estimated by the second term of Eq. (1), resorting to experimentally determined densities [21–23] for the tetraalkylamonium salts, $d_{R_4NNO_3}$, and to the tabulated density [24] for the silver iodide, d_{AgI}.

$$v_1 = v_c - v_s = v_c - \left[\left(\frac{\Delta n_{R_4NNO_3} M_{R_4NNO_3}}{d_{R_4NNO_3}}\right) + \left(\frac{\Delta n_{AgI} M_{AgI}}{d_{AgI}}\right)\right] \quad (1)$$

Table 3
Experimental data and calculated quantities for kinetic runs of reaction system $Et_3N + AgNO_3 + EtI$, based on the reaction in Scheme 1

	Time/s	$[Et_3N]$/M	$[Et_3N]_{corr}$/M	[EtI]/M	$[AgNO_3]_{cal}$/M	[Comp1:1]/M	ln([Comp1:1]/[EtI])
no AgI	0	0.04025	0.04025	0.03805	0.03994	0.03990	0.04736
	76	0.03375	0.03380	0.03160	0.03349	0.03345	0.05697
	153	0.03413	0.03417	0.03198	0.03386	0.03383	0.0563
	269	0.03300	0.03306	0.03086	0.03275	0.03271	0.05832
	539	0.03263	0.03269	0.03049	0.03238	0.03234	0.05902
	792	0.03075	0.03082	0.02863	0.03051	0.03048	0.06281
	1010	0.03056	0.03064	0.02844	0.03033	0.03030	0.0632
	1292	0.02918	0.02926	0.02706	0.02895	0.02892	0.06637
	1511	0.02903	0.02911	0.02692	0.02880	0.02877	0.06673
	1824	0.02783	0.02792	0.02572	0.02761	0.02758	0.06976
	2182	0.02719	0.02728	0.02509	0.02697	0.02695	0.07149
	2609	0.02584	0.02594	0.02374	0.02563	0.02560	0.07545
	3156	0.02393	0.02403	0.02183	0.02372	0.02370	0.08186
	3569	0.02381	0.02392	0.02172	0.02361	0.02359	0.08226
	4134	0.02333	0.02344	0.02124	0.02313	0.02310	0.08408
	4788	0.02280	0.02291	0.02072	0.02260	0.02258	0.08614
	5628	0.02205	0.02217	0.01997	0.02186	0.02183	0.08926
	6349	0.02175	0.02187	0.01967	0.02156	0.02154	0.09057
	7199	0.02138	0.02150	0.01930	0.02119	0.02116	0.09226
	8191	0.02145	0.02157	0.01938	0.02126	0.02124	0.09190
	9237	0.02119	0.02131	0.01912	0.02100	0.02098	0.09311
	10 503	0.02119	0.02132	0.01912	0.02101	0.02099	0.09309
1.0 g AgI	0	0.04025	0.04025	0.03805	0.03954	0.03947	0.03647
	69	0.07571	0.03149	0.02929	0.03078	0.03072	0.04764
	205	0.07570	0.03127	0.02907	0.03056	0.03050	0.04801
	348	0.07557	0.02932	0.02713	0.02862	0.02856	0.05149
	556	0.07533	0.02632	0.02413	0.02562	0.02557	0.05793
	773	0.07527	0.02569	0.02349	0.02498	0.02493	0.05950
	1028	0.07524	0.02539	0.02319	0.02468	0.02463	0.06027
	1273	0.07490	0.02231	0.02011	0.02160	0.02156	0.06946
	1539	0.07479	0.02152	0.01932	0.02081	0.02077	0.07226
	1826	0.07478	0.02145	0.01925	0.02074	0.02070	0.07253
	2134	0.07477	0.02138	0.01918	0.02067	0.02063	0.07280
	2540	0.07475	0.02127	0.01907	0.02056	0.02052	0.07321
	2951	0.07474	0.02116	0.01896	0.02045	0.02041	0.07363
	3447	0.07472	0.02101	0.01881	0.02030	0.02026	0.07420
	4193	0.07466	0.02064	0.01844	0.01993	0.01989	0.07568
	4860	0.07469	0.02083	0.01863	0.02012	0.02008	0.07491
	5732	0.07464	0.02049	0.01829	0.01978	0.01974	0.07627
	6966	0.07464	0.02050	0.01830	0.01979	0.01975	0.07626

In this equation, v_1 stands for the liquid-phase volume and v_c for the volume of reaction mixture collected, $M_{R_4NNO_3}$ and M_{AgI} are the molecular weights of the tetraalkylamonium nitrate and silver iodide, respectively. The final solution volume was obtained by successive iterations of Eq. (1) until a convergence of less than 0.1% on the corrected amine concentration was reached. These calculations showed that the fraction of solid in the collected sample is a minute contribution, which accounts to less than 1% of the total volume over the first 4000 s.

Following all the precautions described above, and having in mind Scheme 1, the concentration for the 1:1 silver–amine coordination compound in solution was obtained resorting to the mass balance equations

$$[AgNO_3]_{tot} = [AgNO_3] + [R_3NAgNO_3] + [(R_3N)AgNO_3] \qquad (2)$$

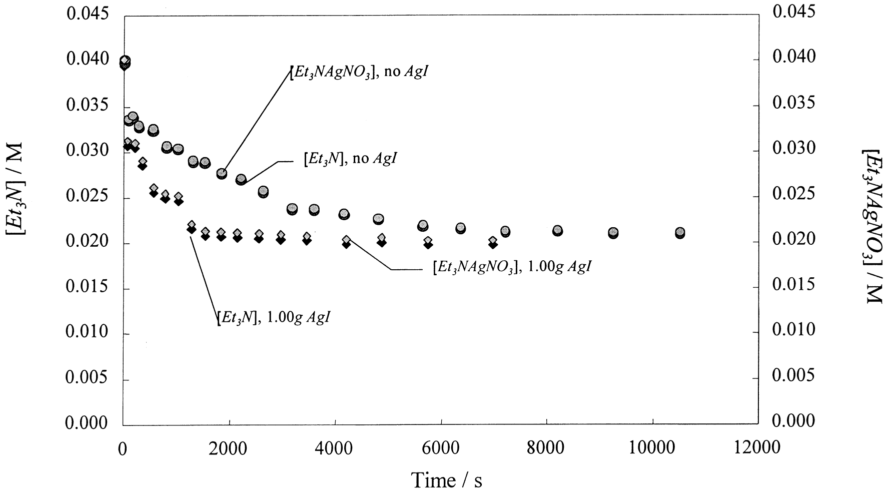


Fig. 1. Plots for the kinetic runs of reaction mixtures 0.04025 ± 0.0002 M in triethylamine, 0.03994 ± 0.0005 M in silver nitrate, and 0.03805 ± 0.0001 M in ethyl iodide obtained in the absence and in the presence of AgI, presented in terms of the experimentally determined amine concentration ($[Et_3N]$) and calculated silver–amine coordination compound concentration ($[Et_3NAgNO_3]$).

and

$$[R_3N]_{tot} = [R_3N] + [R_3NAgNO_3] + 2[(R_3N)_2AgNO_3] \qquad (3)$$

as well as the experimental equilibrium constants

$$K_1 = \frac{[R_3NAgNO_3]}{[AgNO_3][R_3N]} \qquad (4)$$

and

$$K_2 = \frac{[(R_3N)_2AgNO_3]}{[R_3N][(R_3N)AgNO_3]} \qquad (5)$$

where $[AgNO_3]_{tot}$ and $[R_3N]_{tot}$ refer to the total concentration of the silver salt and of the amine under any form in solution, $[AgNO_3]$ and $[R_3N]$ to the free (non-coordinated) silver nitrate and amine concentrations, and $[R_3NAgNO_3]$ and $[(R_3N)_2AgNO_3]$ to the concentrations of the 1:1 and 1:2 silver–amine complexes, respectively.

The resulting third degree polynomial on $[R_3NAgNO_3]$

$$[R_3NAgNO_3]^3 - \left(\left(4K_2(1+K_2) + K_1(2K_2[AgNO_3]_{tot} - 1)\right)K_1K_2\right)[R_3NAgNO_3]^2 - \frac{\left(1 + K_1[R_3N]_{tot} + [AgNO_3]_{tot} + K_1K_2\left([R_3N]_{tot}^2 - 2[R_3N]_{tot}[AgNO_3]_{tot}\right)\right)}{K_1K_2} \times [R_3NAgNO_3] + \frac{[R_3N]_{tot}[AgNO_3]_{tot}}{K_2} = 0 \qquad (6)$$

allows the calculation of the instantaneous concentration of the silver 1:1 complex, provided that $[AgNO_3]_{tot}$ and $[R_3N]_{tot}$ are known. When adsorption is small, Eq. (7), where the subscript 0 refers to beginning of the quaternization reaction $(t=0)$,

$$[AgNO_3]_{tot} = [AgNO_3]_{tot,0} - \left([R_3N]_{tot,0} - [R_3N]_{tot}\right) \qquad (7)$$

holds over all the reaction period and consequently the experimental total amine concentrations, determined any time t, can be used to calculate all the other terms. Eq. (6) was solved by iterative calculation combining incremental search and bracketing methods [25], for every experimental data point, and the calculated instantaneous concentrations of Et_3NAgNO_3 were also plotted in Fig. 1. This plot shows that within the framework of Scheme 1, the amine remains predominantly coordinated in the form of a 1:1 complex, and that the reactivity of the coordination compound is subject to a surface effect by the solid AgI.

Finally, the rate equations for the proposed molecular Scheme 1, including surface and bulk contributions, were developed and tested.

An analysis of reaction Scheme 1, bearing in mind that the species $(R_3N)_2AgNO_3$ is sterically hindered and that $[AgNO_3] \ll [R_3NAgNO_3]$, leads to expression (8) because, under the reaction conditions chosen, more than 95% of the amine is in the form of the 1:1 complex, and, consequently, the contributions due to equilibrium shifts are minor.

$$\frac{d[R_3N]_{total}}{dt} = \frac{d[EtI]_{total}}{dt} \approx \frac{d[R_3NAgNO_3]_{total}}{dt} \qquad (8)$$

where the subscript total refers to the overall concentration: in solution and on the surface.

Therefore, if the solution, as well as surface–solution equilibrium, are maintained throughout [4,26], Eq. (9) may be written as

$$-\frac{d[R_3NAgNO_3]_{total}}{dt} = k_Q[R_3NAgNO_3][EtI] + k'_Q\left(\frac{a_s m}{V}\right)[R_3NAgNO_3]_{ads}[EtI]_{ads} \qquad (9)$$

In this equation, the first term refers to the bimolecular solution reaction and the second term corresponds to the contribution of a Langmuir–Hinshelwood type bimolecular surface reaction (Scheme 1), $[R_3NAgNO_3]_{ads}$ and $[EtI]_{ads}$ stand for the surface concentration of the 1:1 coordination compound and ethyl iodide, which are given by the adequate adsorption isotherms, a_s is the specific surface area, m the mass of adsorbent and V the volume of solution.

Eq. (9) can be simplified and expressed in terms of the initial and instantaneous concentrations of ethyl iodide and silver–amine 1:1 complex, due to the low surface area [9,10,27] of the solid silver iodide.

$$[R_3NAgNO_3] = [R_3NAgNO_3]_{total} - \left(\frac{a_s m}{V}\right)[R_3NAgNO_3]_{ads} \approx [R_3NAgNO_3]_{total} \qquad (10)$$

and

$$[EtI] = [EtI]_{total} - \left(\frac{a_s m}{V}\right)[EtI]_{ads} \approx [EtI]_{total} \qquad (11)$$

The substitution of the terms involving adsorbed species was made bearing in mind that liquid phase catalysis usually involves monolayer adsorption over a set of sites within a narrow range of adsorption energies [4,26,28]. Silver halide catalysis, in particular, either in solvation reactions of alkyl halides or iodo-complexes, as well as amine adsorption, seems to involve Langmuir type adsorption isotherms [3,4,27–32], thus, the surface concentration of ethyl iodide will be given by:

$$[\mathrm{EtI}]_{\mathrm{ads}} = \theta_{\mathrm{EtI}} c_{\mathrm{mono}_{\mathrm{EtI}}} \tag{12}$$

where θ_{EtI} represents the fraction of surface occupied and $c_{\mathrm{mono}_{\mathrm{EtI}}}$ is its monolayer coverage. As amines and alkyl halides both behave as soft Pearson's bases towards the soft superficial silver ions and compete for the same sites, the surface coverage may be equated to

$$[\mathrm{EtI}]_{\mathrm{ads}} = \frac{b_{\mathrm{EtI}}[\mathrm{EtI}]}{1 + b_{\mathrm{R_3N}}[\mathrm{R_3N}] + b_{\mathrm{EtI}}[\mathrm{EtI}]} c_{\mathrm{mono}_{\mathrm{EtI}}} \tag{13}$$

With respect to the molecular species containing silver, an identical type of behaviour is expected and therefore

$$\begin{aligned}[\mathrm{R_3NAgNO_3}]_{\mathrm{ads}} &= \frac{1}{1 + b_{\mathrm{R_3NAgNO_3}}[\mathrm{R_3NAgNO_3}] + b_{\mathrm{AgNO_3}}[\mathrm{AgNO_3}] + b_{\mathrm{(R_3N)_2AgNO_3}}[\mathrm{(R_3N)_2AgNO_3}]} \\ &\quad \times b_{\mathrm{R_3NAgNO_3}}[\mathrm{R_3NAgNO_3}] c_{\mathrm{mono}_{\mathrm{R_3NAgNO_3}}}\end{aligned} \tag{14}$$

For the sake of simplicity, Eq. (9) shall be rewritten as

$$\begin{aligned}\frac{\mathrm{d}x}{\mathrm{d}t} &= k_Q(c-x)(a-x) + k'_Q\left(\frac{a_{\mathrm{s}}m}{V}\right) \\ &\quad \times \left(\frac{b_{\mathrm{R_3NAgNO_3}(c-x)c_{\mathrm{mono}_{\mathrm{R3NAgNO3}}}}}{1 + b_{\mathrm{R_3NAgNO_3}}(c-x)}\right) \\ &\quad \times \left(\frac{b_{\mathrm{EtI}}(a-x)c_{\mathrm{mono}_{\mathrm{EtI}}}}{1 + b_{\mathrm{EtI}}(a-x) + b_{\mathrm{R_3N}}[\mathrm{R_3N}]}\right)\end{aligned} \tag{15}$$

where a and $a-x$ are the initial and instantaneous concentrations of ethyl iodide, respectively, and c and $c-x$ the corresponding initial and instantaneous concentrations of the silver–amine 1:1 complex.

In this final form, Eq. (15) contains two obvious simplifications, namely $b_{\mathrm{AgNO_3}}[\mathrm{AgNO_3}]$ and $b_{\mathrm{(R_3N)_2AgNO_3}}[\mathrm{(R_3N)_2AgNO_3}]$ were neglected when compared with $b_{\mathrm{R_3NAgNO_3}}[\mathrm{R_3NAgNO_3}]$, because in the first case, $[\mathrm{AgNO_3}] \ll [\mathrm{R_3NAgNO_3}]$, and in the second case, the steric hinderance of the 2:1 amine–silver complex allows us to predict that $b_{\mathrm{(R_3N)_2AgNO_3}} \ll b_{\mathrm{R_3NAgNO_3}}$. Eq. (15) can be integrated during a period of time corresponding to constant coverage of the 1:1 silver–amine complex and alkyl halide ($\theta_{\mathrm{R_3NAgNO_3}} = \mathrm{Const}$; $\theta_{\mathrm{EtI}} = \mathrm{Const}'$) as m may also be considered constant due to the small amount of solid formed during the reaction period ($m = m_0 + m(t) \approx m_0$) [4,27,30–32] leading to:

$$\begin{aligned}&\ln\left(\frac{(a+c) - 2x(t) - J}{(a+c) - 2x(t) + J}\right) \\ &\quad = \ln\left(\frac{(a+c) - J}{(a+c) + J}\right) - k_Q Jt\end{aligned} \tag{16}$$

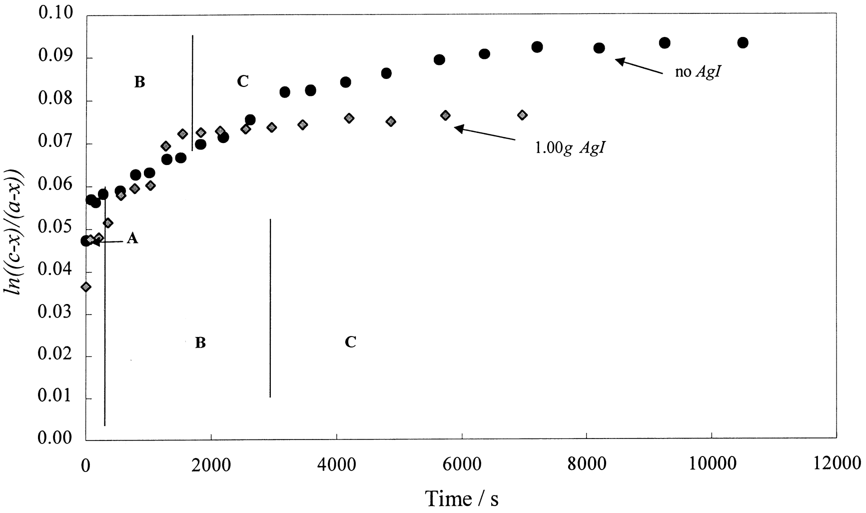


Fig. 2. Plot of the experimental data, according to Eq. (16), obtained for the kinetic runs of reaction mixtures mentioned above (0.04025 ± 0.0002 M · Et_3N + 0.03994 ± 0.0005 M · $AgNO_3$ + 0.03805 ± 0.0001 M · EtI).

where

$$J=\sqrt{(a-c)^2-4\frac{a_s m}{V}\frac{k'_Q}{k_Q}\theta_{\mathrm{R_3NAgNO_3}}c_{\mathrm{mono}_{\mathrm{R_3NAgNO_3}}}\theta_{\mathrm{EtI}}c_{\mathrm{mono}_{\mathrm{EtI}}}} \qquad (17)$$

The second term in Eq. (17) can only be determined by iterative fit, on data pertaining to known initial masses of the catalyst silver iodide. In the absence of an initial mass of the solid catalyst ($m = 0$), Eq. (16) reduces itself to the usual form of an integrated second order rate equation in homogeneous conditions, showing consistency in the deduced expression.

After a relatively long period (t_f), the adsorption for the reacting species ($\theta_{\mathrm{R_3NAgNO_3}} \approx b_{\mathrm{R_3NAgNO_3}}(c-x)$ and $\theta_{\mathrm{EtI}} \approx b_{\mathrm{EtI}}(a-x)$) will be in the low coverage region of the adsorption isotherms, and, consequently, Eq. (15) can be rewritten in a simplified form as

$$\frac{\mathrm{d}x}{\mathrm{d}t}=k_Q(a-x)(c-x)+k'_Q\left(\frac{a_s m}{V}\right)b_{\mathrm{R_3NAgNO_3}} \times(c-x)c_{\mathrm{mono}_{\mathrm{R_3NAgNO_3}}} \times b_{\mathrm{EtI}}(a-x)c_{\mathrm{mono}_{\mathrm{EtI}}} \qquad (18)$$

an equation that upon integration leads to:

$$\ln\left(\frac{c-x(t-t_f)}{a-x(t-t_f)}\right) = \ln\left(\frac{c-x(t_f)}{a-x(t_f)}\right) - k_Q\left(1+\frac{k'_Q a_s m b_{\mathrm{R_3NAgNO_3}}c_{\mathrm{mono}_{\mathrm{R_3NAgNO_3}}}b_{\mathrm{EtI}}c_{\mathrm{mono}_{\mathrm{EtI}}}}{k_Q V}\right) \times(a-c)(t-t_f) \qquad (19)$$

A graphical representation of the experimental data sets in terms of Eq. (16) is presented in Fig. 2. The analysis of this plot is difficult but allows the identification of at least three types of behaviour (A, B and C) with apparent specific velocities successively decreasing, a decrease that is more pronounced in runs initiated in the presence of AgI. It should be mentioned that an identical behaviour was observed in the studies of reaction mixtures containing tributilamine, but in these latter systems, the transitions between these periods occurred more rapidly.

The total inadequacy of the response in terms of the calculated quantities, in particular in terms of the silver–amine complex concentration (Table 3) for extended time periods lead to a re-analysis of reaction Scheme 1, as well as the assumptions underlying the calculations performed.

The accentuated decrease in the quaternization rate, observed in the plots, may be associated with progressive inhibition of the solution and/or surface reactions, as well as with competitive reactions involving any of the species in equilibrium, which have not been accounted for in the model, hypothesis which shall be thoroughly considered next.

(i) Solution inhibition of the quaternization reaction by any of the other species is unlikely, as reaction products are insoluble (AgI, $R'R_3NNO_3$ and $R'R_3NI$), all other reacting species are present in minute concentrations and are not pertinent in terms of the formation of stable intermediates with the 1:1 silver–amine complex. Possible interactions of other silver containing species with the alkyl halide will lead to competing reactions and will be considered latter.

(ii) Surface inhibition of the reaction due to competitive adsorption of other reacting species is also unlikely as the data, collected under various experimental conditions, showed that the phenomena is independent of the concentration of free amine, silver nitrate or alkyl iodide. Surface inhibition due to a decrease in the available surface area associated with product adsorption accompanying precipitation or even co-precipitation [33] of the tetralkyamonium salts is

Table 4
Tests on the aqueous back titration of silver nitrate solutions in toluene containing soluble and insoluble silver salts

υ_{KI}/ml	υ_{Sample}/ml	Composition/M	m_{AgI}/g	m_{R_4NX}/g	υ_{eqv}/ml
5.00	–	–	–	–	1.700
5.00	0.4	Et_3N/0.060	0.01	–	1.700
10.00	0.4	Et_3N/0.060; $AgNO_3$/0.040	0.01	–	1.765
10.00	0.4	Et_3N/0.060; $AgNO_3$/0.040	–	–	1.764
5.00	0.4	EtI/0.060	–	–	1.700
5.00	0.4	EtI/0.060	0.01	–	1.700
5.00	0.4	Bu_3N/0.058	–	–	1.700
5.00	0.4	Bu_3N/0.058	0.01	–	1.700
10.00	0.4	Bu_3N/0.058; $AgNO_3$/0.032	0.01	–	2.092
10.00	0.4	Bu_3N/0.058; $AgNO_3$/0.032	–	–	2.091
10.00	0.4	Bu_3N/0.058; $AgNO_3$/0.032	0.01	0.002 (Bu_4NNO_3)	2.092
5.00	0.4	Bu_3N/0.058 + BuI/0.060	0.01	–	1.700
5.00	0.4	Bu_3N/0.058 + BuI/0.060	–	0.002 (Bu_4NI)	2.372
10.00	0.4 + 0.4	*Bu*$_3$*N*/0.058; *AgNO*$_3$/0.032 + *EtI*/0.060	0.01	–	2.092
10.00	0.4 + 0.4	*Bu*$_3$*N*/0.058; *AgNO*$_3$/0.032 + *EtI*/0.060	–	–	2.091
10.00	0.4 + 0.4	*Bu*$_3$*N*/0.058; *AgNO*$_3$/0.032 + *EtI*/0.060	–	–	2.091[a]
10.00	0.4 + 0.4	*Bu*$_3$*N*/0.058; *AgNO*$_3$/0.032 + *EtI*/0.060	–	–	2.092[b]

$[KI] = 3.327 \times 10^{-3}$ M and $[AgNO_3] = 9.7885 \times 10^{-3}$ M.

[a] Titrated 5 min after the addition of an excess of KI.

[b] Titrated 15 min after the addition of an excess of KI.

Table 5
Set of experimental data, fitted and calculated values for kinetic runs of reaction system $Et_3N + AgNO_3 + EtI$

Time/s	$[AgNO_3]$/M	$[AgNO_3]_{corr}$/M	Time/s	$[Et_3N]$/M	$[Et_3N]_{corr}$/M	$[AgNO_3]_{fit}$/M	[Comp1:1]/M	$[Et_3N]_{free}$/M	[EtI]/M	Run
0	0.03403	0.03403	0	0.03904	0.03904	0.03403	0.03357	0.00457	0.03991	1
85	0.01686	0.01688	118	0.03597	0.03601	0.02300	0.02223	0.01223	0.02888	no AgI
230	0.01671	0.01674	253	0.03412	0.03418	0.01900	0.01825	0.01445	0.02488	
435	0.01716	0.01719	457	0.03268	0.03275	0.01720	0.01651	0.01481	0.02308	
618	0.01634	0.01637	642	0.03227	0.03234	0.01600	0.01532	0.01562	0.02188	
877	0.01503	0.01507	918	0.03104	0.03112	0.01450	0.01387	0.01597	0.02038	
1121	0.01311	0.01315	1143	0.03001	0.03010	0.01350	0.01291	0.01601	0.01938	
1427	0.01155	0.01159	1452	0.02919	0.02929	0.01210	0.01156	0.01666	0.01798	
1821	0.01025	0.01028	1842	0.02857	0.02868	0.01070	0.01020	0.01750	0.01658	
2141	0.00928	0.00931	2153	0.02812	0.02823	0.00980	0.00933	0.01793	0.01568	
2504	0.00874	0.00877	2530	0.02758	0.02770	0.00880	0.00836	0.01846	0.01468	
3029	0.00691	0.00694	3049	0.02721	0.02734	0.00760	0.00721	0.01931	0.01348	
3730	0.00583	0.00586	3750	0.02689	0.02702	0.00640	0.00605	0.02025	0.01228	
4295	0.00497	0.00500	4310	0.02656	0.02670	0.00560	0.00529	0.02079	0.01148	
5218	0.00451	0.00453	5237	0.02610	0.02625	0.00460	0.00434	0.02134	0.01048	
6054	0.00388	0.00390	6075	0.02569	0.02584	0.00400	0.00377	0.02157	0.00988	
6676	0.00356	0.00358	6696	0.02532	0.02548	0.00360	0.00339	0.02169	0.00948	
7467	0.00313	0.00315	7492	0.02518	0.02534	0.00330	0.00311	0.02181	0.00918	
8502	0.00272	0.00274	8517	0.02467	0.02483	0.00290	0.00273	0.02173	0.00878	
10 553	0.00253	0.00255	10 569	0.02446	0.02463	0.00260	0.00000	0.02460	0.00848	
0	0.01686	0.01686	0	0.03904	0.03904	0.01686	0.01595	0.02115	0.03990	2
69	0.01041	0.01042	85	0.03391	0.03395	0.01290	0.01220	0.02040	0.03594	no AgI
180	0.00955	0.00956	198	0.03288	0.03293	0.01090	0.01028	0.02138	0.03394	
389	0.00874	0.00876	408	0.03218	0.03223	0.00920	0.00865	0.02245	0.03224	
678	0.00783	0.00784	694	0.03185	0.03191	0.00800	0.00750	0.02340	0.03104	
938	0.00702	0.00704	956	0.03154	0.03161	0.00720	0.00674	0.02394	0.03024	
1242	0.00630	0.00632	1258	0.03131	0.03138	0.00630	0.00589	0.02469	0.02934	
1524	0.00537	0.00539	1539	0.03102	0.03110	0.00570	0.00532	0.02502	0.02874	
1818	0.00473	0.00474	1835	0.03073	0.03082	0.00510	0.00476	0.02536	0.02814	
2233	0.00398	0.00399	2249	0.03040	0.03050	0.00450	0.00419	0.02569	0.02754	

2759	0.00356	0.00357	2780	0.03015	0.03025	0.00380	0.00354	0.02624	0.02684	
3395	0.00310	0.00311	3414	0.02991	0.03001	0.00310	0.00288	0.02668	0.02614	
4035	0.00240	0.00241	4051	0.02953	0.02965	0.00250	0.00232	0.02692	0.02554	
4586	0.00199	0.00199	4601	0.02937	0.02949	0.00210	0.00195	0.02725	0.02514	
5268	0.00147	0.00147	5312	0.02916	0.02929	0.00170	0.00158	0.02748	0.02474	
5845	0.00139	0.00140	5863	0.02896	0.02909	0.00140	0.00130	0.02760	0.02444	
6583	0.00109	0.00110	6602	0.02875	0.02889	0.00120	0.00111	0.02761	0.02424	
7179	0.00091	0.00092	7196	0.02854	0.02869	0.00110	0.00102	0.02752	0.02414	
8141	0.00104	0.00104	8158	0.02834	0.02849	0.00100	0.00093	0.02743	0.02404	
8601	0.00114	0.00115	8625	0.02813	0.02829	0.00100	0.00000	0.02830	0.02404	
0	0.03413	0.03413	0	0.03854	0.03854	0.03413	0.03372	0.00402	0.03840	3
106	0.01696	0.01705	134	0.03463	0.03483	0.02130	0.02056	0.01276	0.02557	1.5 g AgI
217	0.01665	0.01675	239	0.03356	0.03376	0.01870	0.01797	0.01437	0.02297	
325	0.01618	0.01628	358	0.03291	0.03312	0.01700	0.01629	0.01539	0.02127	
490	0.01583	0.01594	516	0.03184	0.03205	0.01590	0.01523	0.01553	0.02017	
655	0.01545	0.01556	680	0.03076	0.03098	0.01510	0.01447	0.01527	0.01937	
861	0.01447	0.01459	884	0.02883	0.02905	0.01420	0.01365	0.01435	0.01847	
1082	0.01294	0.01305	1108	0.02689	0.02712	0.01310	0.01262	0.01352	0.01737	
1311	0.01180	0.01190	1352	0.02539	0.02561	0.01230	0.01187	0.01287	0.01657	
1641	0.01063	0.01073	1668	0.02474	0.02497	0.01090	0.01049	0.01369	0.01517	
2069	0.00869	0.00878	2093	0.02431	0.02455	0.00960	0.00922	0.01462	0.01387	
2637	0.00742	0.00749	2678	0.02367	0.02391	0.00800	0.00766	0.01556	0.01227	
3312	0.00591	0.00597	3339	0.02302	0.02327	0.00650	0.00621	0.01651	0.01077	
3915	0.00509	0.00514	3944	0.02259	0.02284	0.00570	0.00544	0.01684	0.00997	
4612	0.00446	0.00451	4641	0.02216	0.02242	0.00470	0.00448	0.01748	0.00897	
5340	0.00371	0.00375	5367	0.02195	0.02221	0.00410	0.00390	0.01790	0.00837	
6194	0.00256	0.00259	6225	0.02173	0.02200	0.00340	0.00323	0.01843	0.00767	
8672	0.00232	0.00235	8629	0.02152	0.02179	0.00240	0.00228	0.01928	0.00667	
9288	0.00219	0.00222	9320	0.02130	0.02158	0.00230	0.00218	0.01918	0.00657	
10 417	0.00213	0.00216	10 452	0.02109	0.02138	0.00210	0.00000	0.02140	0.00637	

Table 6
Set of experimental data, fitted and calculated values for kinetic runs of reaction system $Bu_3N + AgNO_3 + EtI$

Time/s	$[AgNO_3]$/M	$[AgNO_3]_{corr}$/M	Time/s	$[Bu_3N]$/M	$[Bu_3N]_{corr}$/M	$[AgNO_3]_{fit}$/M	[Comp1:1]/M	$[Bu_3N]_{free}$/M	[EtI]/M	Run
0	0.03368	0.03368	0	0.03911	0.03911	0.03368	0.03340	0.00511	0.04135	4
62	0.02562	0.02564	77	0.03668	0.03672	0.02880	0.02842	0.00754	0.03647	no AgI
203	0.02350	0.02353	217	0.03649	0.03654	0.02520	0.02472	0.01086	0.03287	
347	0.02305	0.02308	360	0.03630	0.03636	0.02360	0.02310	0.01226	0.03127	
609	0.02091	0.02095	623	0.03611	0.03618	0.02200	0.02148	0.01366	0.02967	
916	0.02261	0.02266	931	0.03592	0.03600	0.02030	0.01977	0.01517	0.02797	
1261	0.01810	0.01814	1276	0.03573	0.03582	0.01820	0.01766	0.01708	0.02587	
1542	0.01594	0.01599	1565	0.03554	0.03565	0.01660	0.01607	0.01852	0.02427	
1891	0.01506	0.01511	1906	0.03543	0.03554	0.01460	0.01409	0.02043	0.02227	
2320	0.01048	0.01052	2335	0.03535	0.03548	0.01250	0.01202	0.02250	0.02017	
2763	0.00905	0.00909	2779	0.03516	0.03530	0.01070	0.01026	0.02416	0.01837	
3359	0.00809	0.00812	3373	0.03497	0.03513	0.00880	0.00841	0.02594	0.01647	
3975	0.00710	0.00714	3997	0.03478	0.03495	0.00750	0.00715	0.02710	0.01517	
4622	0.00629	0.00632	4637	0.03459	0.03477	0.00650	0.00619	0.02796	0.01417	
5440	0.00542	0.00545	5472	0.03440	0.03459	0.00550	0.00523	0.02882	0.01317	
6238	0.00436	0.00439	6256	0.03421	0.03442	0.00470	0.00447	0.02949	0.01237	
7248	0.00340	0.00342	7333	0.03402	0.03424	0.00380	0.00361	0.03025	0.01147	
10 657	0.00225	0.00226	10 588	0.03383	0.03406	0.00230	0.00000	0.03406	0.00997	
11 900	0.00336	0.00339	11 944	0.03364	0.03390	–	–	–	–	
0	0.01885	0.01885	0	0.03872	0.03872	0.01885	0.01818	0.01930	0.04007	5
86	0.01371	0.01372	111	0.03664	0.03667	0.01390	0.01337	0.02224	0.03512	no AgI
216	0.00969	0.00970	241	0.03610	0.03615	0.01110	0.01063	0.02458	0.03232	
406	0.00673	0.00674	442	0.03592	0.03598	0.00830	0.00792	0.02730	0.02952	
601	0.00518	0.00519	617	0.03601	0.03608	0.00680	0.00647	0.02895	0.02802	
828	0.00497	0.00498	841	0.03592	0.03600	0.00580	0.00551	0.02991	0.02702	
1153	0.00491	0.00492	1174	0.03583	0.03592	0.00500	0.00474	0.03066	0.02622	
1402	0.00472	0.00473	1424	0.03574	0.03583	0.00450	0.00426	0.03109	0.02572	
1739	0.00409	0.00410	1754	0.03565	0.03575	0.00410	0.00388	0.03143	0.02532	
2171	0.00355	0.00356	2190	0.03556	0.03567	0.00360	0.00341	0.03188	0.02482	

2683	0.00277	0.00278	2687	0.03538	0.03551	0.00300	0.00284	0.03235	0.02422	
3297	0.00227	0.00228	3309	0.03529	0.03543	0.00250	0.00236	0.03279	0.02372	
3866	0.00204	0.00205	3879	0.03520	0.03535	0.00200	0.00189	0.03324	0.02322	
4580	0.00168	0.00168	4594	0.03502	0.03518	0.00140	0.00132	0.03370	0.02262	
5146	0.00102	0.00103	5163	0.03511	0.03528	0.00100	0.00094	0.03422	0.02222	
5674	0.00030	0.00030	5687	0.03502	0.03520	0.00070	0.00066	0.03446	0.02192	
6469	0.00024	0.00024	6518	0.03485	0.03504	0.00030	0.00000	0.03504	0.02152	
7263	0.00016	0.00016	7278	0.03502	0.03523	0.00000	0.00000	0.00000	0.02122	
8064	−0.00022	–	8087	0.03485	–	–	–	–	–	
0	0.03404	0.03404	0	0.04011	0.04011	0.03404	0.03365	0.00577	0.04135	6
86	0.02423	0.02436	165	0.03748	0.03768	0.02460	0.02406	0.01254	0.03191	1.5 g AgI
252	0.01897	0.01909	275	0.03728	0.03750	0.02220	0.02163	0.01473	0.02951	
465	0.01755	0.01766	479	0.03670	0.03693	0.01890	0.01833	0.01746	0.02621	
668	0.01623	0.01634	684	0.03660	0.03685	0.01700	0.01644	0.01929	0.02431	
877	0.01516	0.01527	893	0.03650	0.03676	0.01570	0.01515	0.02051	0.02301	
1094	0.01426	0.01437	1110	0.03631	0.03658	0.01510	0.01456	0.02094	0.02241	
1348	0.01345	0.01356	1364	0.03621	0.03650	0.01210	0.01161	0.02391	0.01941	
1683	0.01185	0.01195	1699	0.03611	0.03641	0.01120	0.01073	0.02474	0.01851	
2017	0.01026	0.01035	2031	0.03573	0.03604	0.00980	0.00937	0.02581	0.01711	
2515	0.00887	0.00895	2544	0.03534	0.03567	0.00870	0.00831	0.02658	0.01601	
2980	0.00834	0.00842	2997	0.03514	0.03549	0.00760	0.00724	0.02753	0.01491	
3494	0.00755	0.00763	3535	0.03475	0.03511	0.00660	0.00628	0.02819	0.01391	
4117	0.00680	0.00688	4133	0.03436	0.03474	0.00550	0.00523	0.02897	0.01281	
4821	0.00442	0.00447	4835	0.03417	0.03456	0.00490	0.00466	0.02942	0.01221	
5407	0.00425	0.00430	5463	0.03397	0.03438	0.00430	0.00408	0.02986	0.01161	
5913	0.00406	0.00411	5939	0.03378	0.03420	0.00390	0.00370	0.03010	0.01121	
6557	0.00355	0.00360	6593	0.03358	0.03402	0.00350	0.00332	0.03034	0.01081	
7252	0.00316	0.00320	7271	0.03349	0.03394	0.00290	0.00275	0.03089	0.01021	
8427	0.00282	0.00286	8454	0.03329	0.03377	0.00220	0.00208	0.03145	0.00951	
9115	0.00259	–	10526	0.03290	0.03339	0.00220	0.00208	0.03107	0.00911	

also questionable as the process became more prominent with the initial presence of solid AgI in the experimental runs.

(iii) Competitive side reactions, either in solution or on the surface, disregarded in the molecular model proposed initially must be reconsidered under the light of these plots, particularly all the alkyl halide reactions should be considered, namely with the free amine, silver–amine 1:2 complex and free silver nitrate. The reaction of ethyl iodide with the free amines has been studied independently and clearly does not constitute a critical competition [18,19] to the parallel reaction with the 1:1 silver–amine complex. The reaction of the 1:2 silver–amine coordination compound with the alkyl halide should not be significant in solution due to the steric hindrance imposed by six alkyl chains and a nitrate ion around the silver ion and, consequently, even less relevant over a solid surface. A competitive side reaction between dissolved silver nitrate and ethyl iodide was not considered initially due to the minute concentration of the nitrate species ($< 10^{-5}$ M), when compared with the 1:1 silver–amine complex. However, the observed plots may be explained by a rapid side reaction between the alkyl halide and the free silver nitrate, a process that may impose an equilibrium shift towards the silver nitrate, constituting an alternative pathway for R_3NAgNO_3 consumption. This hypothesis seems the most probable explanation for the apparent sharp decrease in the specific velocity for the quaternization reaction when, hypothetically, there should be about 50% of the 1:1 silver–amine complex in the system (Table 3).

The assumption of a competitive side reaction between the free silver nitrate and ethyl iodide involved monitoring simultaneously the amine and silver content [34–36] of the reaction mixture and an experimental set-up for the simultaneous determination of the silver and amine content was assembled [37]. Silver was determined by potentiometric back titration of an excess of standardised potassium iodide and the total amine was analysed as previously described. The reliability the procedure used in the determination of the silver content was checked with synthetic reaction mixtures, as previously

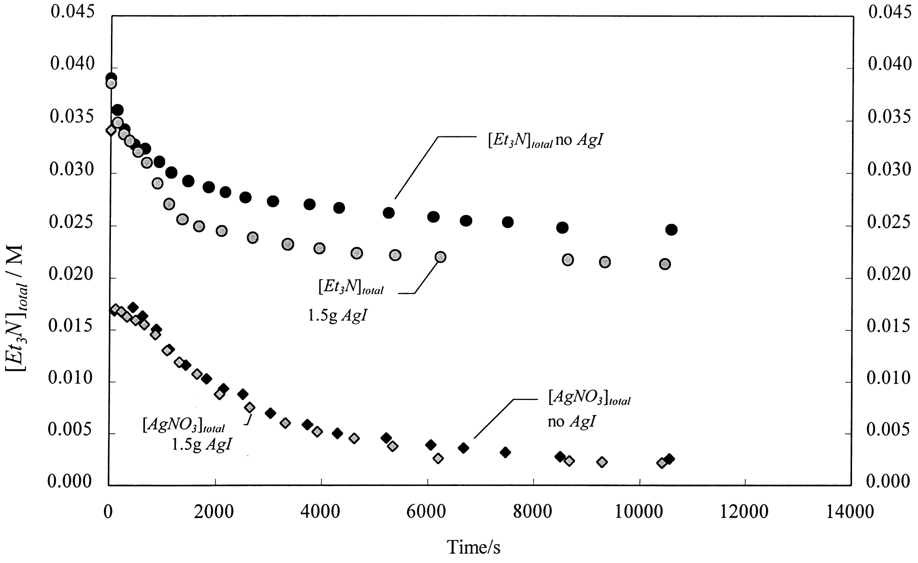


Fig. 3. Plots of the experimental data points obtained, monitoring the total amine and silver nitrate concentrations, for the kinetic run nos. 1 and 3 specified in Table 5.

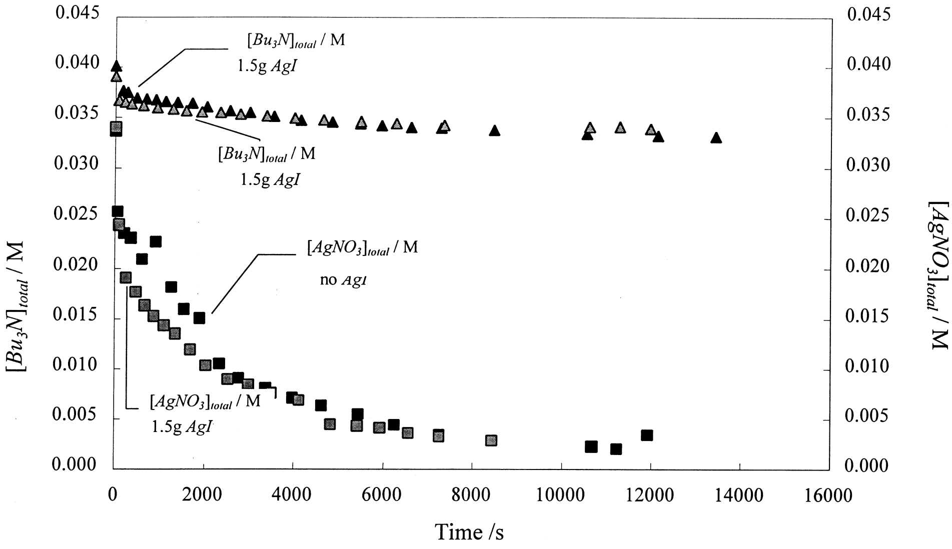
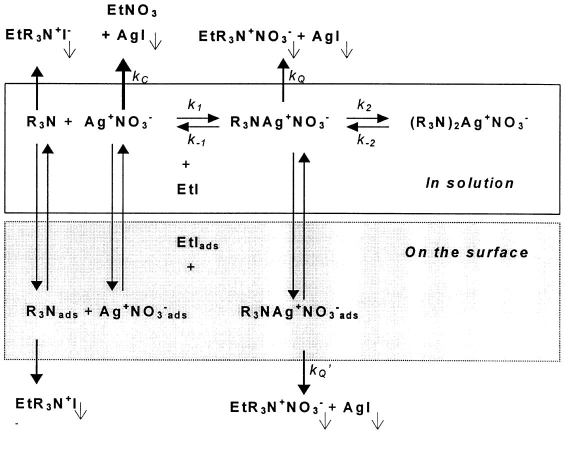


Fig. 4. Plots of the experimental data points obtained, monitoring the total amine and silver nitrate concentrations, for the kinetic run nos. 4 and 6 specified in Table 6.

described for the amines, and the results are presented in Table 4.

The experimental data points obtained in six independent runs and the corresponding calculated quantities are included in Tables 5 and 6. The kinetic runs for some of the reaction mixtures, identified in Tables 5 and 6 (runs 1,3 and 4,6), are plotted in Figs. 3 and 4. These data clearly demonstrate that the rate of consumption of silver is always larger than that of the amine, confirming the hypothesis put forward before, apart from confirming the catalytic effect of the solid AgI at least on the quaternization reaction.



Scheme 2. Schematic representation of the molecular model proposed to interpret the synergistic effect of soluble and insoluble silver salts in the quaternization of tertiary amines by alkyl iodides in aromatic solvents.

In conformity to these additional findings, a competitive solution reaction between the alkyl iodide and the free silver nitrate, with the specific velocity k_C, must be introduced in Scheme 1 and Scheme 2.

As a result, Eqs. (7) and (8) do not hold, and while the first one is no longer necessary, as in these runs where the experimental data provide all the information directly ($[AgNO_3]_{total}$ and $[R_3N]_{total}$), the latter must be rewritten in terms of:

$$\frac{d[R_3N]_{total}}{dt} = \frac{d[R_3N]_{free,total}}{dt} + \frac{d[R_3NAgNO_3]_{total}}{dt} + \frac{d[(R_3N)_2AgNO_3]_{total}}{dt} \qquad (20)$$

and

$$\frac{\mathrm{d}[\mathrm{EtI}]_{\mathrm{total}}}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{AgNO_3}]_{\mathrm{total}}}{\mathrm{d}t} \tag{21}$$

where $[\mathrm{R_3N}]_{\mathrm{free,total}} = [\mathrm{R_3N}] + [\mathrm{R_3N}]_{\mathrm{ads}}$.

Eqs. (21) and (22) are related but not identical, such that Eq. (21) will be given by:

$$\begin{aligned} -\frac{\mathrm{d}[\mathrm{EtI}]_{\mathrm{total}}}{\mathrm{d}t} &= -\frac{\mathrm{d}[\mathrm{AgNO_3}]_{\mathrm{total}}}{\mathrm{d}t} \\ &\approx k_{\mathrm{C}}[\mathrm{EtI}][\mathrm{AgNO_3}] \\ &\quad + k_Q[\mathrm{R_3NAgNO_3}][\mathrm{EtI}] \\ &\quad + k'_Q\left(\frac{a_{\mathrm{s}}m}{V}\right)[\mathrm{R_3NAgNO_3}]_{\mathrm{ads}}[\mathrm{EtI}]_{\mathrm{ads}} \end{aligned} \tag{22}$$

and, consequently,

$$\begin{aligned} -\frac{\mathrm{d}[\mathrm{EtI}]_{\mathrm{total}}}{\mathrm{d}t} &= -\frac{\mathrm{d}[\mathrm{AgNO_3}]_{\mathrm{total}}}{\mathrm{d}t} \\ &\approx \left(\frac{k_{\mathrm{C}}}{K_1[\mathrm{R_3N}]} + k_Q\right)[\mathrm{R_3NAgNO_3}][\mathrm{EtI}] \\ &\quad + k'_Q\left(\frac{a_{\mathrm{s}}m}{V}\right)[\mathrm{R_3NAgNO_3}]_{\mathrm{ads}}[\mathrm{EtI}]_{\mathrm{ads}} \end{aligned} \tag{23}$$

Solving Eq. (23) involves variable transformations, prior to integration, as the rate of consumption for the species involved in the catalysed quaternization ($[\mathrm{R_3NAgNO_3}]$ and [EtI]) is not identical. A preliminary analysis of the dependencies underlying these rate equations clearly shows that the reaction rate for the ethyl halide is always larger than the rate of amine consumption.

Furthermore, expression (23) also discloses the previously mentioned dependencies on the concentration of uncoordinated amine ($[\mathrm{R_3N}]$) and on the amine chain length through the first equilibrium constant for the solution silver–amine coordination (K_1). The dependency on the mass of AgI is also accounted for in this expression as the contribution of the surface reaction depends linearly on the mass of solid.

Eq. (23) unveils many potentialities in terms of the description of the overall process, but its integration is difficult due to the complex relations between the rates of amine and halide consumption. Nonetheless, estimates for some of the relevant kinetic parameters can be calculated from the data obtained so far as an approximate relation between the concentrations of the 1:1 silver–amine complex and the total silver nitrate can be established. In fact, resorting to the mass balance equation for the total silver content, the equations for the solution equilibrium constants (Eqs. (4) and (5)), and bearing in mind the low surface area of the solid, it is possible to write:

$$\begin{aligned} -\frac{\mathrm{d}[\mathrm{AgNO_3}]_{\mathrm{total}}}{\mathrm{d}t} &= -\left(1 + \frac{1}{K_1[\mathrm{R_3N}]} + K_2[\mathrm{R_3N}]\right) \\ &\quad \times \frac{\mathrm{d}[\mathrm{R_3NAgNO_3}]_{\mathrm{total}}}{\mathrm{d}t} \end{aligned} \tag{24}$$

Consequently and resorting to Eq. (21), one may conclude that

$$\begin{aligned} -\frac{\mathrm{d}[\mathrm{AgNO_3}]_{\mathrm{total}}}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{EtI}]_{\mathrm{total}}}{\mathrm{d}t} &\cong -(1 + K_2[\mathrm{R_3N}]) \\ &\quad \times \frac{\mathrm{d}[\mathrm{R_3NAgNO_3}]_{\mathrm{total}}}{\mathrm{d}t} \end{aligned} \tag{25}$$

as the second term in the parenthesis of Eq. (24) is neglectable ($\approx 10^{-5}$). This simple approximate relation allows the integration of Eq. (23) whenever a period of time, with an almost constant free amine concentration ($[\mathrm{R_3N}] \cong \overline{[\mathrm{R_3N}]}$), may be identified within a kinetic run.

A close look at Tables 5 and 6 allows the identification of the onset of such periods of

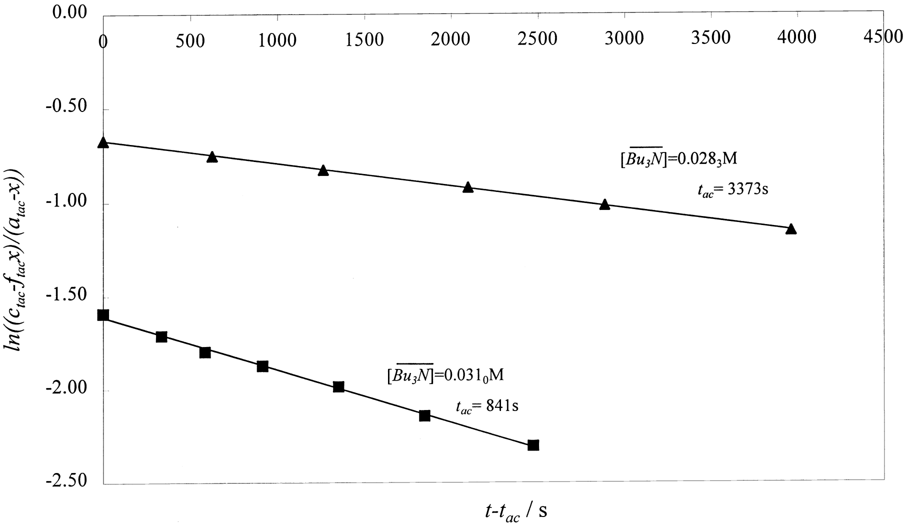


Fig. 5. Plots of Eq. (28) for the experimental data points obtained in kinetic run nos. 4 and 5.

time at different instants (t_{ac}), which depend on the set of initial conditions an on the nature of the amine. For $t \geq t_{ac}$,

$$\frac{1}{(1+K_2\overline{[\mathrm{R_3N}]}})\times x = f_{t_{ac}}x \tag{26}$$

where x is the decrease in the ethyl iodide concentration, $f_{t_{ac}}$ is the constant relative to the period of time when $\overline{[\mathrm{R_3N}]} =$ constant and $f_{t_{ac}}$ x the corresponding decrease in the 1:1 silver–amine complex concentration.

Eq. (23) can be expressed in terms of the concentration of the 1:1 silver–amine complex for $t = t_{ac}(c_{t_{ac}})$, as well as the corresponding ethyl iodide concentration ($a_{t_{ac}}$),

$$\begin{aligned}\frac{\mathrm{d}x}{\mathrm{d}t_{t\geq t_{ac}}} \cong {} & \left(k_Q + \frac{k_\mathrm{C}}{K_1\overline{[\mathrm{R_3N}]}}\right)\\ & \times\left(a_{t_{ac}}-x\right)\left(c_{t_{ac}}-f_{t_{ac}}x\right)\\ & + k'_Q\left(\frac{a_\mathrm{s}m}{V}\right)b_{\mathrm{R_3NAgNO_3}}\\ & \times\left(c_{t_{ac}}-f_{t_{ac}}x\right)c_{\mathrm{mono}_{\mathrm{R_3NAgNO_3}}}\\ & \times b_{\mathrm{EtI}}\left(a_{t_{ac}}-x\right)c_{\mathrm{mono}_{\mathrm{EtI}}}\end{aligned} \tag{27}$$

This equation will describe approximately the period where there is a constant contribution from the competitive reaction ($t \geq t_{ac}$) of the alkyl halide with the free silver nitrate and, therefore, by integration, one obtains:

$$\begin{aligned}&\ln\left(\frac{c_{t_{ac}}-f_{t_{ac}}x}{a_{t_{ac}}-x}\right)\\ &\quad = \ln\left(\frac{c_{t_{ac}}}{a_{t_{ac}}}\right) - \left(k_Q + \frac{k_\mathrm{C}}{K_1\overline{[\mathrm{R_3N}]}}\right)\\ &\quad\times\left(1+\frac{k'_Q a_\mathrm{s} m b_{\mathrm{R_3NAgNO_3}} c_{\mathrm{mono}_{\mathrm{R_3NAgNO_3}}} b_{\mathrm{EtI}} c_{\mathrm{mono}_{\mathrm{EtI}}}}{k_Q V}\right)\\ &\quad\times\left(a_{t_{ac}}-f_{t_{ac}}c_{t_{ac}}\right)\left(t-t_{ac}\right)\end{aligned} \tag{28}$$

Fig. 5 shows plots of Eq. (28) for runs 4 and 5, and evidences that the approximations previ-

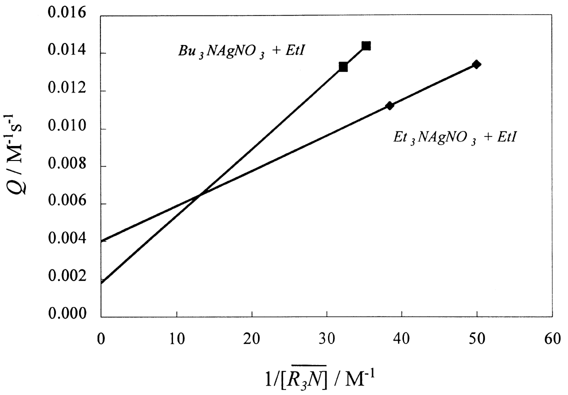


Fig. 6. Plots of the calculated Q factors in terms of $1/\overline{[\mathrm{R_3N}]}$, for $t \geq t_{ac}$, in kinetic run nos. 1,2 and 4,5, initiated in the absence of solid.

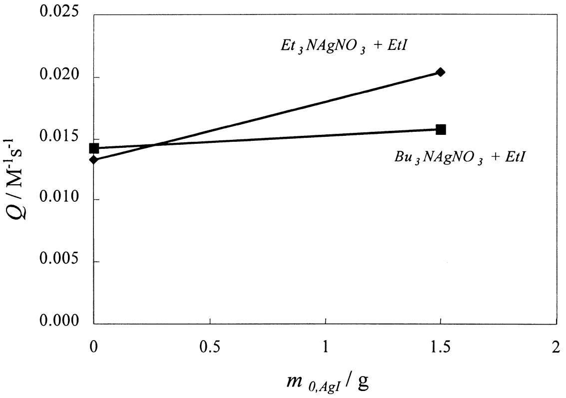


Fig. 7. Plots of calculated Q factors in terms of the initial mass of AgI, for $t \geq t_{ac}$, in kinetic run nos. 1,3 and 5,6.

ously made are acceptable and that the t_{ac} values are appropriately chosen.

An analysis of the slopes of the plots of Eq. (28) becomes clearer using a simplified notation, namely introducing the factor $Q(Q = -\text{slope}/(a_{t_{ac}} - f_{t_{ac}} c_{t_{ac}}))$ for $t \geq t_{ac}$

$$Q = \left(k_Q + \frac{k_C}{K_1[\overline{R_3N}]}\right) \times \left(1 + \frac{k'_Q a_s m b_{R_3NAgNO_3} c_{\mathrm{mono}_{R_3NAgNO_3}} b_{EtI} c_{\mathrm{mono}_{EtI}}}{k_Q V}\right) \quad (29)$$

From this expression, values of k_C and k_Q may be easily extracted from runs initiated without solid catalyst by plotting Q vs. $1/[\overline{R_3N}]$ (Fig. 6). Runs 1,2 and 4,5 (where $m_0 = 0$) were used for this purpose. These plots show the expected dependencies, namely the intercept (k_Q) is smaller for the bulkier amine (Bu_3N), but the slope (k_C/K_1)of the plot is larger for this same amine ($K_1(Bu_3N) = 7.9 \times 10^6$ and $K_1(Et_3N) = 2.9 \times 10^7$ [6]).

Plots for the dependence of Q on m_{AgI}, concerning Q values obtained with similar free amine concentrations (runs 1,3 and 4,6) are presented in Fig. 7, and clearly substantiate the enhancement of the coordinated amine quaternization rate due to the solid.

4. Conclusions

The calculated solution rate constants for the quaternization reactions, k_Q, $k_{Et_3NAgNO_3+EtI} = 4.0 \times 10^{-3}$ M^{-1} s^{-1} and $k_{Bu_3NAgNO_3+EtI} = 1.8 \times 10^{-3}$ M^{-1} s^{-1} (Table 7), are slightly overestimated, as for $t \geq t_{ac}$, the mass of solid is no longer zero, nonetheless, these values display an unquestionable rate increase of about 10^3 times over the corresponding rates in the absence of soluble silver ($k_{Et_3N+EtI} = 3.3 \times 10^{-6}$ M^{-1} s^{-1} [18,19]; $k_{Bu_3N+EtI} = 6.2 \times 10^{-7}$ M^{-1} s^{-1}). Apart from this, it should be pointed out that the coordination reduces the sterical hindrance of the longer alkyl chains to the nucleophilic attack of the ethyl iodide in solution as $k_Q(Et_3NAgNO_3)/k_Q(Bu_3NAgNO_3) \cong 2$ while the corresponding ratio for the uncoordinated amines is 5.

The rate constant estimates for the fast competitive reaction, k_C, proposed in Scheme 2 are 5.8×10^3 M^{-1} s^{-1} and 2.8×10^3 M^{-1} s^{-1} (Table 7). These values constitute an important

Table 7
Set of conditions chosen, as well as calculated values for k_Q and k_C from the kinetic runs where the total amine and silver nitrate compositions were simultaneously monitored

System	t_{ac}/s	$[\overline{R_3N}]$/M	Q/M^{-1} s^{-1}	k_Q/M^{-1} s^{-1}	k_C/M^{-1} s^{-1}	Run no.
$Et_3N + AgNO_3 + EtI$	1842	0.020	0.0134 0.0112	4.0×10^{-3}	5.8×10^3	1
$Et_3N + AgNO_3 + EtI$	408	0.026				2
$Et_3N + AgNO_3 + EtI$	1668	0.017	0.0204	–	–	3
$Bu_3N + AgNO_3 + EtI$	3373	0.028	0.0142 0.0132	1.8×10^{-3}	2.8×10^3	4
$Bu_3N + AgNO_3 + EtI$	841	0.0310				5
$Bu_3N + AgNO_3 + EtI$	1364	0.028	0.0158	–	–	6

parameter derived in this work and pertain to the reaction between silver nitrate and ethyl iodide in toluene that has never been reported before.

In respect to the surface contribution in this complex process, and despite the fact that adsorption parameters for the reacting species are not available in the literature, it is possible to conclude that, as expected, the surface effect is smaller for the bulkier amine, namely coordinated tributilamine.

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