JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 10, 600–606 (1997)

SOLVOLYSIS–DECOMPOSITION OF *N*-1-ADAMANTYL-*N*-*p*-TOLYLCARBAMOYL CHLORIDE IN HYDROXYLIC SOLVENTS†

DENNIS N. KEVILL* AND VEENA UPADHYAY
Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115–2862, USA

In hydroxylic solvents, *N*-1-adamantyl-*N*-*p*-tolylcarbamoyl chloride undergoes a facile rate-determing ionization with very little assistance from nucleophilic solvation (very low sensitivity to changes in solvent nucleophilicity). In the relatively nucleophilic aqueous ethanol or aqueous acetone, the cation formed reacts directly with the solvent. In fluoroalcohols, the low nucleophilicity of the solvent allows an effective competition from a pathway involving disproportionation to the 1-adamantyl cation and *p*-tolyl isocyanate, followed by reaction of the new cation either with solvent or with the chloride ion formed in the initial ionization. Grunwald–Winstein plots against Y_{C1} values show for different binary solvent systems a marked dispersion, which can be considerably reduced by incorporation into the analyses of a term governed by the aromatic ring parameter. (*I*). © 1997 John Wiley & Sons, Ltd.

J. Phys. Org. Chem. **10**, 600–606 (1997) No. of Figures: 3 No. of Tables: 1 No. of References: 33

Keywords: N-1-adamantyl-*N*-*p*-tolylcarbamoyl chloride; solvolysis; decomposition; hydroxylic solvents

Received 27 December 1996; revised 21 February 1997; accepted 3 March 1997

INTRODUCTION

It has been demonstrated[1] that reaction of 1-adamantyl chloroformate (1-AdOCOCl) proceeds, in a wide variety of hydroxylic solvents, almost exclusively with loss of carbon dioxide, accompanied by capture of the 1-adamantyl cation by either a nucleophilic solvent component or the previously formed chloride ion. Only in ethanol was a small ($<1\%$) component involving formation of the 1-adamantyl alkyl carbonate, *via* nucleophilic displacement at the acyl carbon, observed. In contrast, 1-adamantyl fluoroformate (1-AdOCOF) gave exclusively solvolysis–decomposition products only in highly ionizing solvents, usually also of low nucleophilicity, and in other solvents appreciable attack at acyl carbon accompanied this process.[2] The movement towards nucleophilic displacement at the acyl carbon was considered to be a consequence of the large chloride/fluoride leaving group effects in S_N1 reactions[3] and the small corresponding effects in addition–elimination reactions at the acyl carbon.[4]

Attention has recently been given to the solvolyses of carbamoyl chlorides,[5–7] where the alkoxy or aryloxy group of the chloroformate is replaced by an *N*,*N*-disubstituted amino group. Reports that the reactions proceed predominantly by S_N1 pathways[8a–e] have been confirmed. However when the extended Grunwald–Winstein equation:

$$\log (k/k_0) = lN_T + mY_{C1} + c \qquad (1)$$

was applied, sensitivities to solvent nucleophilicity changes (l values) in the range of 0·33–0·74 suggested an appreciable nucleophilic contribution,[8f] rationalized as a nucleophilic solvation of the developing carbocation. In equation (1), k and k_0 are the specific rates of solvolysis in the solvent under consideration and in 80% ethanol, respectively, l is the sensitivity to changes in solvent nucleophilicity (N_T),[9] m is the sensitivity towards changes in solvent ionizing power (Y_{C1})[10] and c is a constant (residual) term.

Combining aspects of the two above-mentioned types of study, it is of interest to see whether an *N*,*N*-disubstituted carbamoyl chloride in which one of the substituents is a 1-adamantyl group would give mechanisms involving loss of an isocyanate ester ($R{-}N{=}C{=}O$), paralleling the loss of carbon dioxide from 1-AdOCOCl. Indicating that such a mechanism might be possible is the previous observation that pyrolysis of *N*-*tert*-butyl-*N*-alkylcarbamoyl chlorides can lead to high yields of the corresponding alkyl isocyanate,[11] when the substrate is heated either as a melt or in a non-hydroxylic solvent such as toluene, 1,2-dichloroethane, 1,1,2-trichloroethane or nitrobenzene. In a related process, arylcarbamoyl chlorides (ArNHCOCl) lose HCl

---

Correspondence to: D. N. Kevill.

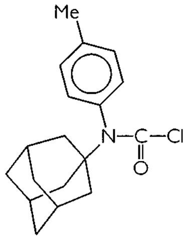
†Abstracted, in part, from the MS thesis of Veena Upadhyay, Northern Illinois University, May 1993.

Contract Grant Sponsor: NATO Collaboration. Grant No. 921261

CCC 0894–3230/97/080600–07 $17.50

spontaneously to give the aryl isocyanate.[12]

In the present study, there are practical advantages to introducing an aryl group as the second substituent on the nitrogen. The arylamine then produced after subsequent loss of carbon dioxide from the 1-Ad(Ar)NCOOH product (resulting *via* replacement of chloride by the water component of an aqueous–organic solvent) will be neutral under the titration conditions,[5] unlike dialkylamines, which behave as bases and neutralize the equivalent amount of acid that is produced.[6,7] The secondary (1-adamantyl)arylamines required for reaction with the phosgene to give the corresponding carbamoyl chloride have previously been synthesized[13] by the interaction of 1-bromoadamantane with a large excess of the appropriate primary arylamine at 170–180 °C. It was found[13] that the use of *p*-toluidine led to a large preference for nitrogen alkylation over aromatic-ring alkylation. Accordingly, we chose to synthesize *N*-1-adamantyl-*N*-*p*-tolylcarbamoyl chloride (**1**) and then study both its kinetic behavior and its tendency to lose tolyl isocyanate when dissolved in a variety of hydroxylic solvents.



1

EXPERIMENTAL

Materials. Acetone, ethanol and methanol were purified as described previously.[14] The purifications of 1,1,1,3,3,3-hexafluoro-2-propanol[15] (HFIP) and 2,2,2-trifluoroethanol (TFE)[16] were also performed using previously reported procedures. 1-Adamantyl *p*-toluenesulfonate was prepared[14,17] from 1-adamantanol (Aldrich) *via* 1-adamantyl iodide.[14,18] 1-Adamantyl chloride (Aldrich, 98%) was used as received, and 1-adamantyl 2,2,2-trifluoroethyl ether[19,20] and 1-adamantyl 1,1,1,3,3,3-hexafluoro-2-propyl ether[20] were prepared by previously reported procedures.

N-1-Adamantyl-N-p-tolylamine. A 1·5 g sample of 1-adamantyl *p*-toluenesulfonate and 0·80 g of *p*-toluidine were heated in an ampule at 80 °C for 12 h. The contents were then added to 150 ml of boiling 0·05 M HCl. After filtration, the filtrate was cooled and NaOH solution added until alkaline. The precipitated amine was removed by filtration and recrystallized from ethanol to give 0·25 g (21%) of product, m.p. 96–98 °C (lit.[13] 98–98·5 °C).

N-1-Adamantyl-N-p-tolylcarbamoyl chloride. A solution of 0·33 g of *N*-1-adamantyl-*N*-*p*-tolylamine and 0·16 g of pyridine were dissolved in 3·0 ml of toluene and this was slowly added, with stirring, to 1·5 ml of an ice-cooled 20% solution of phosgene in toluene (Fluka). After completion of the addition, the solution was stirred for 72 h. The solvent was removed under vacuum and the solid residue extracted into diethyl ether. After filtration, the ether was removed under vacuum to give a solid product, which was recrystallized from hexane to yield 0.31 g (75%) of product, m.p. 123–126 °C; IR (KBr disc) includes peaks at 2917, 2858, 1749, 1518, 1201, 732 and 648 cm^{-1}; ^{1}H NMR (CDCl$_3$), δ (p.p.m.) 1·8–2·2 (m, 15 H), 2·37 (s, 3H), 7.01 (d, $J=8$ Hz, 2H), 7·17 (d, $J=8$ Hz, 2H). Analysis: calculated for $C_{18}H_{22}NClO$, C 71·17, H 7·25, N 4·62, Cl 11·67; found, C 71·25, H 7·37, N 4·52, Cl 11·13%.

Kinetic studies. The kinetic runs and subsequent regression analyses were carried out as described previously.[9a]

Product studies. Response-calibrated gas–liquid partition chromatography using a Hewlett-Packard Model 5840A instrument with a flame ionization detector and numerical integration capabilities was used. A glass column (Alltech, 6 ft × 1/4 in), packed with 15% Carbowax 20M on 80–100-mesh Chromosorb W NAW, was used in a programmed temperature cycle with nitrogen as the carrier gas.

RESULTS

Kinetic studies

These were carried out primarily at 0·0 °C. For methanol, ethanol and the two aqueous ethanol mixtures, runs were also performed at 25·0 °C and, for the two pure alcohols, also at two additional temperatures, so as to give four data points for the calculation of the enthalpy and entropy of activation. The specific rates of solvolysis in the above-mentioned solvents and also in 2-propanol, 90% methanol, 90–70% acetone (three compositions) and in three 2,2,2-trifluoroethanol–ethanol mixtures are reported in Table 1, where the activation parameters are given in a footnote.

Product studies

The analysis concentrated on the products which would be formed after loss of *p*-tolyl isocyanate: 1-adamantyl chloride together with either 1-adamantyl 1,1,1,3,3,3-hexafluoro-2-propyl ether in HFIP or 1-adamantyl 2,2,2-trifluoroethyl ether in TFE. To determine the actual percentages produced, internal (response-calibrated) standards were added; these were adamantane for solvolyses in TFE and 1-adamantyl 2,2,2-trifluoroethyl ether for solvolyses in HFIP.

A 0·0039 M solution of substrate in freshly purified HFIP was allowed to react for 5 min at 25·0 °C and the products were found to include 31% of the ether and 34% of 1-adamantyl chloride. The corresponding reaction in HFIP–water (97:3, w/w) gave only 4·9% of the ether and 2·3% of

1-adamantyl chloride.

A semiquantitative determination in TFE gave a specific rate of solvolysis of about $7\times10^{-3}\ \mathrm{s}^{-1}$ at 0·0 °C, corresponding to a half-life of about 2 min. Accordingly, reaction for 7 min at 25·0 °C would be in excess of 10 half-lives, and after this time the products contained 85% of the ether and only 0·6% of 1-adamantyl chloride. After 10 min the percentage of the chloride had risen to 1·1% and it continued to rise such that, in an experiment with an initially 0·0020 M substrate concentration, it had reached 14%, together with 86% of the ether, after 3060 min and 16% with 85% of the ether after 5730 min.

In ethanol, 80% ethanol, 80% acetone and 70% acetone, the half-life can be estimated from the measured specific rates (Table 1) and the products were examined after reaction at 25·0 °C for 10 half-lives. During this time only a little solvolysis of any 1-adamantyl chloride product would occur, since this material solvolyzes about 100 times slower than **1**[10a] In none of these solvents was any 1-adamantyl chloride observed and no 1-adamantyl ethyl ether[14] was detected in either ethanol or 80% ethanol.

Table 1. First-order rate coefficients for the solvolysis of *N*-1-adamantyl-*N*-*p*-tolylcarbamoyl chloride[a] in a series of pure and binary solvents, of solvent ionizing power value Y_{C1}

Solvent[b]	Temperature (°C)	$10^5\,k\ (\mathrm{s}^{-1})$[c]	Y_{C1}[d]
100% EtOH[3]	0·0	0·94 ± 0·04	− 2.5
	25·0	30·9 ± 1·5	
	35·0	94·1 ± 6·7	
	45·0	276 ± 23	
90% EtOH	0·0	3·66 ± 0·17	− 0·9
	25·0	154 ± 8	
80% EtOH	0·0	7·29 ± 0·42	0·00
	25·0	315 ± 24	
i-PrOH	25·0	4·50 ± 0·12	
100% MeOH[e]	0·0	12·4 ± 0·4	− 1·2
	15·0	114 ± 4	
	25·0	347 ± 10	
	35·0	1120 ± 20	
90% MeOH	0·0	48 ± 2·7	− 0·2
90% Acetone	0·0	0·229 ± 0·015	− 2·2
80% Acetone	0·0	1·24 ± 0·10	− 0·8
70% Acetone	0·0	3·26 ± 0·16[f]	0·17
60T–40E[g]	0·0	181 ± 13	0·64
40T–60E	0·0	27·8 ± 1·6	− 0·44
20T–80E	0·0	5·28 ± 0·14	− 1·42

[a] Concentration 0·0039 M.

[b] Except where indicated otherwise, the other component is water and the percentage quoted is (by volume) that of the organic component.

[c] With associated standard deviation.

[d] From Ref. 10.

[e] Using the data at the four temperatures, the activation parameters (with standard errors) are, for 100% EtOH, $\Delta H_{298}^{\ddagger} = 21{\cdot}3 \pm 0{\cdot}3$ kcal mol^{-1} and $\Delta S_{298}^{\ddagger} = -3{\cdot}3 \pm 1{\cdot}3$ eu and, for 100% MeOH, $\Delta H_{298}^{\ddagger} = 20{\cdot}9 \pm 0{\cdot}6$ kcal mol^{-1} and $\Delta S_{298}^{\ddagger} = 0{\cdot}1 \pm 2{\cdot}1$ eu (1 kcal = 4·184 kJ).

[f] In the presence of 0·0030 M *n*-Bu$_4$NCl, a value of 2·39 (± 0·14) $\times 10^{-5}\ \mathrm{s}^{-1}$ was observed.

[g] T–E refer to 2,2,2-trifluoroethanol–ethanol mixtures (by volume).

DISCUSSION

To avoid the high temperatures of 170–180 °C previously used[13] for the adamantylation of primary amines, we made use of the very high $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ leaving group ratio for 1-adamantyl derivatives[21] (about 10^4) and, by substituting the *p*-toluenesulfonate for the bromide, we were able to carry out the reaction at 80 °C. The procedure for converting the secondary amine in to the carbamoyl chloride was closely related to that used previously[22] for converting 1-adamantanol into the chloroformate.

By extrapolating the specific rate data measured at 0–45 °C (Table 1), one can arrive at a value for ethanolysis at 50·0 °C of $494\times10^{-5}\ \mathrm{s}^{-1}$. This places the reactivity relative to simple *N*,*N*-dialkylcarbamoyl chlorides intermediate between the values for the diethyl derivative ($66{\cdot}6\times10^{-5}\ \mathrm{s}^{-1}$) and the diisopropyl derivative ($3420\times10^{-5}\ \mathrm{s}^{-1}$).[8e] That this is due to the counterbalancing influences of a large acceleration due to introduction of a tertiary alkyl group and a potentially large deceleration due to introduction of an aryl group can be seen from a comparison with the diphenyl derivative, where the value of $0{\cdot}057\times10^{-5}\ \mathrm{s}^{-1}$ at 62·5 °C[5] can be compared with an extrapolated value for ethanolysis of **1** of $1760\times10^{-5}\ \mathrm{s}^{-1}$, a specific rate difference of 3×10^4.

Stepanov and Stolyarov[13] compared the chemical and physical behaviors of *N*,*N*-disubstituted arylamines involving two methyl groups with the corresponding properties when one of these methyl groups was replaced by a 1-adamantyl group. For the *N*-(1-adamantyl)-*N*-methylarylamines, electrophilic attack by the benzenediazonium ion or by the nitrosonium ion did not occur, the pK_{a} values for the conjugate acids were substantially increased and in the UV spectra the peak at about 250 nm showed a bathochromic shift, associated with a considerable reduction in the extinction coefficient. These three differences were very plausibly explained in terms of steric hindrance to conjugation by the bulky 1-adamantyl group, such that the aromatic ring cannot be planar relative to the other two substituents on the nitrogen. In compound **1**, there is a closely related situation, with the *N*-methyl group being replaced by the carbonyl chloride (COCl) grouping, and the about 10^4 increase in reactivity on replacing a phenyl group by a 1-adamantyl group will arise not only from the electronic effect of introducing a tertiary alkyl group but also from the reduction in the ground-state stabilization that is associated with the remaining phenyl group, this reduction resulting from the steric hindrance to it attaining the favored coplanar arrangement.

For the solvolyses in methanol and ethanol, entropies of activation of close to zero are observed (+0·1 eu in methanol and −3·3 eu in ethanol). These are only slightly

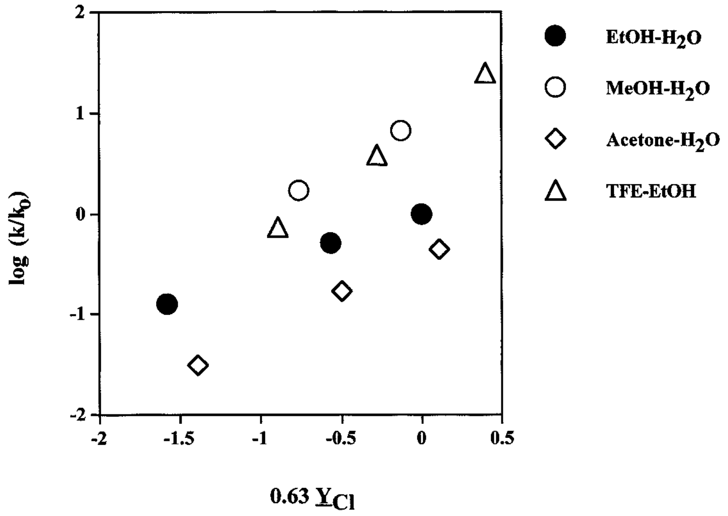
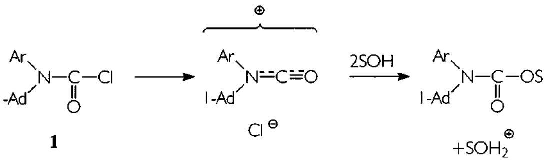


Figure 1. Plot of log (k/k_0) for solvolyses of **1** against Y_{Cl} values

less positive than the values of +3·3 and 6·3 eu for corresponding alcoholyses of 1-adamantyl chloroformate, a reaction believed to involve ionization accompanied by loss of carbon dioxide.[1] The solvolyses of *N*,*N*-dimethylcarbamoyl chloride have been postulated as being S_N1 in character[8] but with appreciable nucleophilic solvation of the developing cation;[5] this requires an appreciable ordering of solvent molecules, reflected in the entropies of activation being more negative (−8·0 and −14·3 eu).[5] The alcoholyses of ethyl chloroformate are believed to involve a well defined bimolecular attack by the solvent and the entropies of activation are considerably more negative (−34·4 and −33·7 eu).[23] While entropy of activation values must be interpreted with caution, the large variations observed for these systems are consistent with the other evidence presented, indicating that the alcoholyses of **1** proceed by an ionization mechanism with little, if any, nucleophilic solvation of the incipient cation at the transition state.

Application of the one-term Grunwald–Winstein equation [equation (1) without the lN_T term] to the 11 specific rates of solvolysis of **1** at 0·0 °C led to a plot with considerable dispersion for the different binary systems (Figure 1) and a low correlation coefficient of 0·745. The slope (m) is 0·63±0·19 and c=0·42±0·58. Use of the full equation (1) gave essentially no improvement with a multiple correlation coefficient (R) of 0·756 and l=0·36±0·64 (probability of 0·59 that the lN_T term is statistically insignificant), m=0·71±0·24 and c=0·54±0·60. Clearly, the dispersion is not caused by a contribution to the overall linear free energy relationship from the lN_T term. A poorly defined l value using equation (1) frequently results from the need to incorporate a term governed by the aromatic ring parameter (I).[24] This parameter can be used to correct for dispersions observed in Grunwald–Winstein treatments which result from influences other than solvent nucleophilicity. The effects are observed in the presence of π electrons, most usually of aromatic rings. It has been proposed[25] that the parameter is governed by a combination of differential solvation and ion-pair return effects, and a scale of I values was developed based on a comparison of the specific rates of solvolysis of the *p*-methoxybenzyldimethylsulfonium ion and the 1-adamantyldimethylsulfonium ion.

Previously, the aromatic ring parameter has been found to be important only for benzylic-type systems[26] or when anchimeric assistance involving migration of an aryl group to an electron-deficient carbon is operative.[24] In the present case [equation (2)], a resonance-stabilized carbocation intermediate is produced, which can be captured by solvent. The aromatic ring is adjacent to a nitrogen carrying a partial positive charge, but this is an atom which maintains its electron octet.



(2)

A treatment using the equation

$$\log(k/k_0) = mY_{Cl} + hI + c \qquad (3)$$

where h is the sensitivity to changes in the value for the aromatic ring parameter (I) as the solvent is varied,[25] gives a very good correlation (Figure 2) with, for the 11 solvents, R=0·9883, m=0·54±0·05, h=1·86±0·15 and

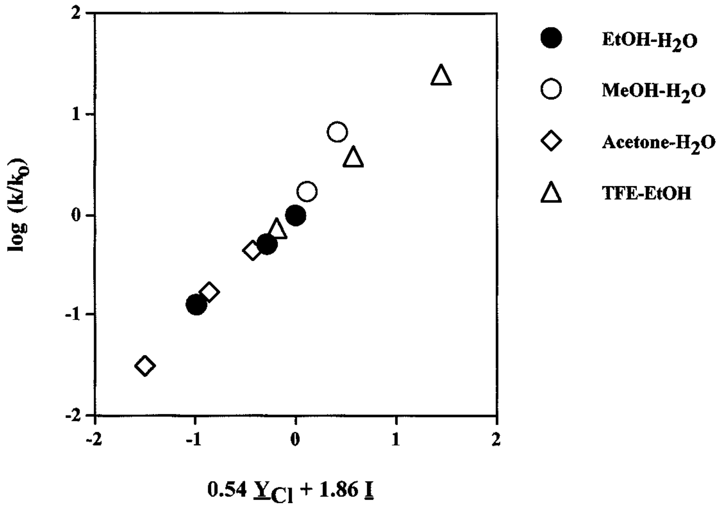


Figure 2. Plot of log (k/k_0) for solvolyses of **1** against $mY_{Cl}+hI$

$c=0\cdot08\pm0\cdot14$. The relevance of the h parameter here is very interesting, in view of the previous belief[24–26] that its use should be restricted to studies of benzylic systems or related systems involving 1,2-aryl migration. Although it would be unwise to make far-reaching conclusions based on one study in a limited range of solvents, this observation does suggest that further consideration of the range of reaction types for which the hI parameter can usefully be incorporated into the Grunwald–Winstein treatment would be worthwhile.

An alternative approach would be in terms of similarity models, comparing with a well defined system involving S_N1 solvolysis at the acyl carbon of an acyl halide. The solvolysis of anisoyl chloride, although containing the electron-releasing *p*-methoxy group, appears to be weakly susceptible to nucleophilic assistance from the solvent[27,28] and 2,6-dimethylbenzoyl chloride,[28] with bimolecular attack sterically hindered,[29] constitutes a better model. The 2,6-dimethylbenzoyl chloride is also similar in that its high reactivity is associated with a rotation of the aryl group[30] and reduced resonance stabilization of the ground state; this is an effect suggested in this paper as also being applicable to solvolyses of **1**.

As previously presented[28] plot of the specific rates of solvolysis of 2,6-dimethylbenzoyl chloride against Y_{Cl} values ($m=0\cdot79\pm0\cdot07$; $r=0\cdot9540$) for solvolyses in aqueous acetone, aqueous ethanol and aqueous methanol (14 solvents) shows a dispersion which superficially parallels that (Figure 1) for solvolyses of **1** in these binary solvents. The specific rates of solvolysis of this acyl chloride can also be treated in terms of equation (3), with values of $0\cdot89\pm0\cdot03$ for m, $1\cdot45\pm0\cdot20$ for h and $0\cdot09\pm0\cdot15$ for c, with a multiple correlation coefficient (R) of 0·99231. The absence of any significant nucleophilic solvation is nicely confirmed by an analysis carried out with addition of the lN_T term[9] to equation (3). This leads to essentially no improvement over use of equation (3), with the multiple correlation coefficient increasing only to 0·99234 and the F-test value falling from 353 to 215. The sensitivity values obtained are $-0\cdot07\pm0\cdot36$ for l (with a probability that the lN_T term is insignificant of 0·85), $0\cdot88\pm0\cdot05$ for m, $1\cdot51\pm0\cdot40$ for h and $0\cdot08\pm0\cdot16$ for c.

It has been shown in Grunwald–Winstein treatments that a good similarity model must have an h/m ratio very similar in value to that for the solvolysis under consideration.[24–26] Despite related dispersion patterns, the h/m values for solvolyses of **1** (3·44) and of 2,6-dimethylbenzoyl chloride (1·63) differ appreciably and a direct LFER plot of the log (k/k_0) values for the two substrates, in eight solvents, shows only a fair correlation (Figure 3), with a slope of $0\cdot79\pm0\cdot12$, an intercept of $0\cdot22\pm0\cdot27$ and a correlation coefficient of 0·936.

No 1-adamantyl chloride product was detected in 80% or 70% aqueous acetone and neither this compound nor 1-adamantyl ethyl ether[14] was detected in 100–80% aqueous ethanol. It appears that, in these solvents, the carbamoyl cation formed from **1** in the rate-determining step is captured by solvent molecules sufficiently rapidly that it does not have the opportunity to disproportionate and the pathway illustrated in equation (2) is followed.

The capture of the cation formed from **1** will be slower in solvents rich in fluoroalcohol, which are of considerably reduced solvent nucleophilicity,[9] and a loss of *p*-tolyl isocyanate to give the 1-adamantyl cation followed by a collapse with chloride ion or capture by solvent can now be observed [equation (4)].

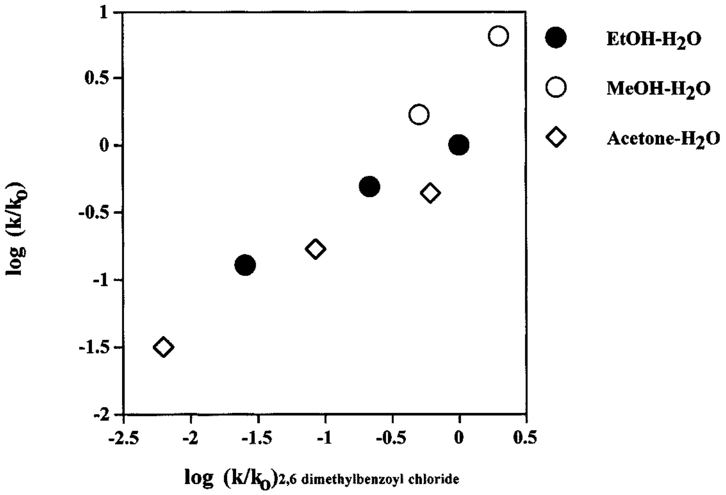
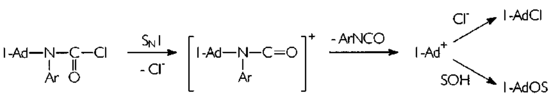


Figure 3. Plot of log (k/k_0) for solvolyses of **1** against log (k/k_0) for solvolyses of 2,6-dimethylbenzoyl chloride



(4)

In 2,2,2-trifluoroethanol, at 25·0 °C, an 85% yield of 1-adamantyl 2,2,2-trifluoroethyl ether was obtained, together with only a very small amount (<1%) of 1-adamantyl chloride. The small amount of 1-adamantyl chloride formed in TFE is in contrast to a 42% yield from the corresponding reaction of 1-adamantyl chloroformate.[1] Possible major factors in this difference include the slower disproportionation of the cation from **1** than that from 1-adamantyl chloroformate, indicated by the observation that 1-AdOCOCl gives entirely disproportionation even in aqueous acetone and aqueous ethanol solvents, which completely capture the cation from **1** prior to its disproportionation. With a longer lifetime for the cation, increased separation of the chloride ion will occur, favoring, after disproportionation, capture by solvent. The increased bulk, and accompanying increased difficulty in migrating into the solvent cage, of *p*-tolyl isocyanate relative to carbon dioxide could also increase the extent to which the chloride ion is shielded from the 1-adamantyl cation after any disproportionation within the ion-pair stage.

The increasing amounts of 1-adamantyl chloride, 15% after 3 days from an initially 0·002 M solution of **1**, are consistent with the equilibrations observed in solvolyses of 1-adamantyl halides in fluoroalcohols. Such equilibrations can be avoided by addition of a base such as pyridine,[20] 2,6-lutidine[19,31] or 2,4,6-collidine.[32] Unfortunately, such additions to solvolyses of **1** would lead to a rapid conversion of the substrate to the corresponding pyridinium chloride, which would then be the material whose solvolysis was studied.[33]

In 1,1,1,3,3,3-hexafluoro-2-propanol, the solvent nucleophilicity is even lower and there is increased opportunity firstly for disproportionation to follow the initial ionization and, second, for diffusion away of the *p*-tolyl isocyanate. Further, the very low nucleophilicity of the solvent then leads to considerably increased amounts (34%) of 1-adamantyl chloride being formed in the competition between chloride ion and solvent for the 1-adamantyl cation.

CONCLUSIONS

Both the kinetics and the product studies are consistent with the formation from **1**, in an ionization process, of the corresponding carbamoyl cation (1-AdArNCO)$^+$. Owing primarily to steric effects, the process involves very little nucleophilic solvation, as shown by the negligible *l* value, and it proceeds rapidly because steric crowding forces a rotation of the aryl group. This destabilizes the ground state due to the enforced reduction in the resonance interaction with the lone pair of electrons on the nitrogen.

In the solvents of reasonable nucleophilicity, the carbamoyl cation unites with a solvent molecule but, in fluoroalcohols of low nucleophilicity, disproportionation to an adamantyl cation and *p*-tolyl isocyanate dominates. This is indicated by the detection in the products of 1-adamantyl fluoroalkyl ethers and, especially in 1,1,1,3,3,3-hexafluoro-2-propanol, 1-adamantyl chloride, formed by capture of the 1-adamantyl cation by fluoroalcohol or chloride ion, respectively.

ACKNOWLEDGMENTS

D. N. K. thanks Dr T. W. Bentley (University of Wales, Swansea, UK) for hospitality and helpful discussions during the preparation of this manuscript. We thank Dr Malcolm J.

D'Souza (University of Wisconsin Center–Waukesha County) for helpful discussions and assistance with the regression analyses.

REFERENCES

1. D. N. Kevill, J. B. Kyong and F. L. Weitl, *J. Org. Chem.* **55**, 4304 (1990).
2. D. N. Kevill and J. B. Kyong, *J. Org. Chem.* **57**, 258 (1992).
3. (a) C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.* **75**, 246 (1953); (b) B. D. Song and W. P. Jencks, *J. Am. Chem. Soc.* **111**, 8470 (1989).
4. (a) M. Green and R. F. Hudson, *J. Chem. Soc.* 1055 (1962); (b) A. Queen and T. A. Nour, *J. Chem. Soc., Perkin Trans. 2* 935 (1976); (c) S. I. Orlov, A. L. Chimishkyan and M. S. Grabarnik, *J. Org. Chem. (USSR), Engl. Ed.* **19**, 1981 (1983).
5. M. J. D'Souza, D. N. Kevill, T. W. Bentley and A. C. Devaney, *J. Org. Chem.* **60**, 1632 (1995).
6. D. N. Kevill, A. J. Oldfield and M. J. D'Souza, *J. Chem. Res. (S)* 122 (1996).
7. D. N. Kevill, A. J. Casamassa and M. J. D'Souza, *J. Chem. Res. (S)* 472 (1996).
8. (a) H. K. Hall, Jr, *J. Am. Chem. Soc.* **77**, 5993 (1955); (b) H. K. Hall, Jr, and C. H. Lueck, *J. Org. Chem.* **28**, 2818 (1963); (c) I. Ugi and F. Beck, *Chem. Ber.* **94**, 1839 (1961); (d) A. Queen, *Can. J. Chem.* **45**, 1619 (1967); (e) R. Bacaloglu, C. Dăescu and G. Ostrogovich, *J. Chem. Soc., Perkin Trans. 2* 1011 (1972); (f) S. C. Kim, H.-B. Song and I. Lee, *J. Korean Chem. Soc.* **23** 368 (1979).
9. (a) D. N. Kevill and S. W. Anderson, *J. Org. Chem.* **56**, 1845 (1991); (b) D. N. Kevill, in *Advances in Quantitative Structure–Property Relationships,* edited by M. Charton, Vol. 1, pp. 81–115. JAI Press, Greenwich, CT (1996).
10. (a) T. W. Bentley and G. E. Carter, *J. Am. Chem. Soc.* **104**, 5741 (1982); (b) T. W. Bentley and G. Llewellyn, *Prog. Phys. Org. Chem.* **17**, 121 (1990); (c) D. N. Kevill and M. J. D'Souza, *J. Chem. Res. (S)* 174 (1993); (d) J. S. Lomas, M. J. D'Souza and D. N. Kevill, *J. Am. Chem. Soc.* **117**, 5891 (1995).
11. J. N. Tilley and A. A. R. Sayigh, *J. Org. Chem.* **28**, 2076 (1963).
12. R. Bacaloglu and C. A. Bunton, *Tetrahedron* **29**, 2721 (1973).
13. F. N. Stepanov and Z. E. Stolyarov, *J. Org. Chem. (USSR), Engl. Ed.* **5**, 537 (1969).
14. D. N. Kevill, K. C. Kolwyck and F. L. Weitl, *J. Am. Chem. Soc.* **92**, 7300 (1970).
15. T. W. Bentley, C. T. Bowen, W. Parker and C. I. F. Watt, *J. Chem. Soc., Perkin Trans. 2* 1244 (1980).
16. Z. Rappoport and J. Kaspi, *J. Am. Chem. Soc.* **96**, 4518 (1974).
17. D. N. Kevill and C.-B. Kim, *J. Org. Chem.* **39**, 3085 (1974).
18. P. v. R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.* **83**, 2700 (1961).
19. J. Kaspi and Z. Rappoport, *J. Am. Chem. Soc.* **102**, 3829 (1980).
20. B. Allard and E. Casadevall, *Nouv. J. Chim.* **9**, 725 (1985).
21. T. W. Bentley and K. Roberts, *J. Org. Chem.* **50**, 4821 (1985).
22. W. L. Haas, E. V. Krumkalns and K. Gerzon, *J. Am. Chem. Soc.* **88**, 1988 (1966).
23. A. Kivinen, *Acta Chim. Scand.* **19**, 845 (1965).
24. D. N. Kevill and M. J. D'Souza, *J. Chem. Soc., Perkin Trans 2*, 257 (1997).
25. D. N. Kevill, N. HJ Ismail and M. J. D'Souza, *J. Org. Chem.* **59**, 6303 (1994).
26. (a) D. N. Kevill and M. J. D'Souza, *Org. React. (Tartu)* **29**, 55 (1995); (b) D. N. Kevill and M. J. D'Souza, *J. Chem. Res. (S)* 286; (*M*) 1649 (1996); (c) D. N. Kevill and M. J. D'Souza, *J. Chem. Soc., Perkin Trans. 2* 973 (1995); (d) D. N. Kevill, S. W. Anderson and N. HJ Ismail, *J. Org. Chem.* **61**, 7256 (1996); (e) I. Lee, H. J. Koh and B. D. Chang, *Bull. Korean Chem. Soc.* **16**, 1104 (1995).
27. T. W. Bentley and H. C. Harris, *J. Chem. Soc., Perkin Trans. 2* 619 (1986).
28. T. W. Bentley, H. C. Harris and I. S. Koo, *J. Chem. Soc., Perkin Trans. 2* 783 (1988).
29. M. L. Bender and M. C. Chen, *J. Am. Soc.* **85**, 30 (1963).
30. D. Leibfritz, *Chem. Ber.* **108**, 3014 (1975).
31. (a) V. J. Shiner, Jr, W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky and M. W. Rapp, *J. Am. Chem. Soc.* **91**, 4838 (1969); (b) T. Ando and S. Tsukamoto, *Tetrahedron Lett.* 2775 (1977); (c) S. P. McManus and S. E. Zutaut, *Tetrahedron Lett.* **25**, 2859 (1984).
32. B. Allard, A. Casadevall, E. Casadevall and C. Largeau, *Nouv. J. Chim.* **4**, 539 (1980).
33. S. L. Johnson and H. M. Giron, *J. Org. Chem.* **37**, 1383 (1972).