Kinetics and Mechanism of the Decomposition of 1-Adamantyl Chloroformate[1]

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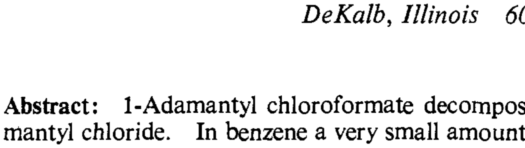
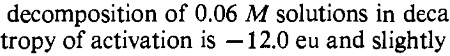
Abstract: 1-Adamantyl chloroformate decomposes in decane or in the molten phase to give exclusively 1-adamantyl chloride. In benzene a very small amount of acid formation occurs, 0.5% at 54.2°, and a 94% yield of 1-adamantyl chloride has been isolated. Increased, but still small, amounts of acid production accompany decomposition in nitrobenzene and mixtures of nitrobenzene with benzene. From a reaction with silver hexafluoroantimonate in nitrobenzene, 1-(*m*-nitrophenyl)adamantane was isolated and characterized. At 54.2°, the relative rates of decomposition of 0.06 *M* solutions in decane, benzene, and nitrobenzene are 1:1260:205,000. In benzene, the entropy of activation is −12.0 eu and slightly less negative values are obtained in nitrobenzene and benzene–nitrobenzene mixtures; similar values have been reported for S_N1 solvolyses of 1-adamantyl halides. In nitrobenzene, tetra-*n*-butylammonium chloride modestly accelerates the decomposition, and the extent of acid formation decreases in a manner consistent with the rate of solvolysis in the absence of added chloride (3.0% at 15.0°) being equal to the rate of production of dissociated 1-adamantyl carbonium ions.

The mechanisms of $\mathrm{S_Ni}$ decomposition of solutions of alkyl chloroformates and related esters, such as chlorosulfinates and chloroglyoxalates, have usually been expressed in terms of either cyclic or tight ion-pair processes, with the possibility of a continuous spectrum of mechanisms intermediate between the two extremes.[3]

The covalent process can be expressed



and the ionic process



$$\mathrm{RO}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{Cl} \longrightarrow \mathrm{R^+O^-}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{Cl} \longrightarrow \mathrm{R^+Cl^-} + \mathrm{CO_2} \searrow \mathrm{RCl}$$

In the decomposition of various *para*-substituted α-phenylethyl chloroformates, a large negative Hammett ρ value was interpreted in terms of a tight ion-pair mechanism.[4] Also, a covalent process will show only a moderate response to variation in solvent-ionizing power, while an ionic process will show a large increase in rate as the solvent-ionizing power increases.[5] For example, although the decomposition of α-trifluoromethylallyl chlorosulfinate, at about 100°, has a rate variation of only sevenfold in going from decane to nitrobenzene;[6] the rate of decomposition of α-methylallyl chloroformate, at 75.0°, varies by a factor of about 10,000 in going from decane to nitrobenzene.[3d]

In a consideration of ionic decomposition processes, it would be advantageous to study *t*-alkyl chloroformates. *t*-Butyl chloroformate has been prepared at low temperatures,[7] but it was found to decompose rapidly above 10° and with formation, in addition to carbon dioxide, of isobutylene and hydrogen chloride, rather than *t*-butyl chloride.

Recently, 1-adamantyl chloroformate, a bridgehead tertiary chloroformate, was prepared.[8] This chloroformate has extremely desirable characteristics for the study of ionic decomposition processes in that it has a tertiary structure and, due to substitution being at a bridgehead, the decomposition product will be exclusively 1-adamantyl chloride. Also, rearside nucleophilic participation by external chloride ion[9] is sterically excluded. A convenient titration technique is available for determining the extent of decomposition since 1-adamantyl chloroformate solvolyzes rapidly in aqueous acetone to produce a proportionate amount of acid and the 1-adamantyl chloride, which has been formed during decomposition, is unreactive under these conditions.

Results

Decomposition in Benzene–Nitrobenzene Mixtures. The rates of decomposition were determined at approximately 10° temperature intervals in benzene, nitrobenzene, and four benzene–nitrobenzene mixtures. The results are summarized in Table I. For benzene solutions, runs performed in glass flasks, glass flasks packed with glass wool or Teflon (a polytetrafluoroethylene) lined vessels gave essentially identical reaction rates.

The first-order rate coefficients reported within Table I can be used to calculate the enthalpy and entropy of activation for each of the six solvent compositions. These parameters are summarized in Table II.

Decomposition in Decane. A 0.06 *M* solution contained within a Teflon-lined vessel at 54.2° decomposed

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

[2] Graduate School Fellow, 1966–present; Petroleum Research Fund Fellow, summer 1967.

[3] (a) D. J. Cram, *J. Am. Chem. Soc.*, 75, 332 (1953); (b) S. Winstein and G. C. Robinson, *ibid.*, 80, 169 (1958); (c) S. H. Sharman, F. F. Caserio, R. F. Nystrom, J. C. Leach, and W. G. Young, *ibid.*, 80, 5965 (1958); (d) K. L. Oliver and W. G. Young, *ibid.*, 81, 5811 (1959); (e) E. S. Lewis and W. C. Herndon, *ibid.*, 83, 1955, 1959, 1961 (1961); (f) S. J. Rhoads and R. E. Michel, *ibid.*, 85, 585 (1963).

[4] K. B. Wiberg and T. M. Shryne, *ibid.*, 77, 2774 (1955).

[5] S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, 83, 618 (1961).

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[7] A. R. Choppin and J. W. Rodgers, *ibid.*, 70, 2967 (1948).

[8] W. L. Haas, E. V. Krumkalns, and K. Gerzon, *ibid.*, 88, 1988 (1966).

[9] D. N. Kevill, G. H. Johnson, and W. W. Neubert, *Tetrahedron Letters*, 3727 (1966).

Table I. First-Order Rate Coefficients (sec^{-1}) for the Decomposition of 0.06 *M* 1-Adamantyl Chloroformate in Benzene–Nitrobenzene Mixtures[a]

Temp, °C	Solvent composition (wt % PhNO$_2$) 100	80	60	40	20	0
64.7				4.38×10^{-3}	1.50×10^{-3}	1.78×10^{-4}
54.2	1.06×10^{-2}	6.43×10^{-3}	4.16×10^{-3}	1.89×10^{-3}	5.48×10^{-4}	6.53×10^{-5}
45.0	5.04×10^{-3}	2.51×10^{-3}	1.72×10^{-3}	7.50×10^{-4}	2.33×10^{-4}	2.03×10^{-5}
34.5	1.67×10^{-3}	9.41×10^{-4}	5.39×10^{-4}	2.40×10^{-4}	6.94×10^{-5}	6.70×10^{-6}
25.0	6.06×10^{-4}	3.20×10^{-4}	1.74×10^{-4}	7.39×10^{-5}	2.14×10^{-5}	2.09×10^{-6}
14.6	1.82×10^{-4}	9.09×10^{-5}	4.45×10^{-5}	2.18×10^{-5}	5.83×10^{-6}	5.51×10^{-7}
0.0		1.14×10^{-5}	6.19×10^{-6}			

[a] The standard error for the first-order rate coefficient associated with each run was typically 2–4%, but it was slightly higher for a few of the faster runs.

Table II. Enthalpies ($\Delta H^{\ddagger}$) and Entropies ($\Delta S^{\ddagger}_{298}$) of Activation for Decomposition of 1-Adamantyl Chloroformate in Various Benzene–Nitrobenzene Mixtures[a]

Wt % PhNO$_2$	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}_{298}$, eu
100	18.77 ± 0.15	−10.29 ± 0.54
80	20.11 ± 0.16	−7.06 ± 0.56
60	20.89 ± 0.07	−5.65 ± 0.28
40	20.13 ± 0.17	−9.90 ± 0.63
20	20.87 ± 0.12	−9.87 ± 0.43
0	21.61 ± 0.17	−12.03 ± 0.59

[a] Errors quoted are standard errors.

Table III. Effect of Concentration on First-Order Rate Coefficient for Decomposition, k_1 (sec^{-1})

[$C_{10}H_{15}OCOCl$], *M*	Decane at 64.7°, 10^7k_1	Benzene at 54.2°, 10^6k_1	Nitrobenzene at 25.0°, 10^4k_1
0.06	3.97 ± 0.24	6.53 ± 0.03	6.06 ± 0.11
0.12	6.91 ± 0.89	6.74 ± 0.15	5.71 ± 0.08
0.18	9.64 ± 0.95	6.95 ± 0.11	6.50 ± 0.09

Table IV. Effect of Added Tetra-*n*-butylammonium Chloride upon the First-Order Rate Coefficient for Decomposition of 0.06 *M* 1-Adamantyl Chloroformate in Nitrobenzene at 25.0°

[*n*-Bu_4NCl], *M*	0.0000	0.0247	0.0494	0.0988	0.1976
10^4k_1, sec^{-1}	6.06 ± 0.11	6.80 ± 0.13	7.57 ± 0.15	9.11 ± 0.12	10.20 ± 0.69

only to the extent of 20% during 47 days. Decompositions in Pyrex glass vessels were modestly catalyzed by the addition of Pyrex glass wool. Runs were found to be reproducible when performed in Teflon-lined vessels and addition to one run of a substantial amount of shredded Teflon caused only a 16% increase in rate (combined standard error being 12%). For a 0.06 *M* solution, the first-order rate coefficient was 5.16 (±0.26) × 10^{-8} sec^{-1} at 54.2° and 3.96 (±0.24) × 10^{-7} sec^{-1} at 64.7°.

Effect of 1-Adamantyl Chloroformate Concentration on Decomposition Rates. The results reported above were all obtained for 0.06 *M* solutions. The effect of varying the concentration was studied in benzene, nitrobenzene, and decane. Quite large variations were observed in decane, small variations in benzene, and no discernible trend in nitrobenzene (Table III).

Effect of Added Tetra-*n*-butylammonium Chloride upon the Decomposition Rate in Nitrobenzene. A study at 25.0° showed a modest increase in the decomposition rate with increase in the added tetra-*n*-butylammonium chloride concentration (Table IV).

Product Studies. From decomposition of 1-adamantyl chloroformate in benzene at 54.2°, a 94% yield of high purity 1-adamantyl chloride was isolated. Consistent with the absence of any appreciable interaction with the solvent, infinity titers showed the presence of only a trace of acid. The infinity acid titer for a glass wool catalyzed decomposition in decane was zero.

Infinity titers indicated the presence of only small amounts of acid formation (<3.0%) accompanying decompositions either in nitrobenzene or in benzene–nitrobenzene mixtures. It would appear that the acid development must be accompanied by alkylation of the nitrobenzene or of the benzene within benzene–nitrobenzene mixtures; alkylation of nitrobenzene by the 1-adamantyl carbonium ion was shown to be feasible by the isolation and characterization of 1-(*m*-nitrophenyl)adamantane from a reaction of 1-adamantyl chloroformate with silver hexafluoroantimonate in nitrobenzene, at room temperature.[10]

Acid Production Accompanying Decomposition. The extent of any solvolysis accompanying the decomposition reaction can be determined on the basis of solvolytic reaction being accompanied by acid development. Determinations of the acid concentration at complete reaction of the 1-adamantyl chloroformate were made for several temperatures and solvent compositions. The results are summarized in Table V.

Table V. Percentage of Total Reaction of 0.093 *M* 1-Adamantyl Chloroformate Proceeding with Acid Formation in Benzene–Nitrobenzene Mixtures

Temp, °C		Wt % of C_6H_6 0[c]	20	40	60	80	100
25.0	Titer[a]	0.21	0.19	0.14	0.10	0.06	
	% acid[b]	2.5	2.3	1.7	1.2	0.7	
45.0	Titer[a]	0.18	0.16	0.13	0.07	0.05	0.06
	% acid[b]	2.2	1.9	1.6	0.8	0.6	0.7
64.7	Titer[a]	0.13	0.12	0.08	0.04	0.04	0.04[d]
	% acid[b]	1.6	1.5	1.0	0.5	0.5	0.5[d]

[a] Average of three titers of 0.0111 *M* methanolic NaOMe per 1.00-ml aliquot after completion of reaction at appropriate temperature. [b] Infinity acid concentration relative to initial concentration of 1-adamantyl chloroformate. [c] Also, 3.0% acid at 15.0°. [d] Corresponding titer of 0.16 ml and acid production of 1.9% in toluene.

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(10) This technique has also been used to prepare 1-(*m*-nitrophenyl)-apocamphane; R. J. Trancik and P. Beak, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract S164.

A study was also made of the effect of added tetra-*n*-butylammonium chloride upon the amount of acid production accompanying the decomposition of 0.093 *M* 1-adamantyl chloroformate in nitrobenzene. These results are summarized in Table VI.

Table VI. Acid Production Accompanying Decomposition of 0.093 *M* 1-Adamantyl Chloroformate in Nitrobenzene at 15.0°

$10^3[n\text{-Bu}_4\text{NCl}]$, *M*	0.00	2.58	5.16	7.74	23.2
Titer,[a] ml	3.83	3.46	3.30	2.97	2.42
% acid	3.05	2.74	2.62	2.36	1.92

[a] Titer of 0.00222 *M* methanolic NaOMe per 3.00-ml aliquot.

Discussion

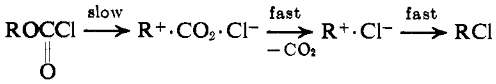
The decomposition has characteristics consistent with an ionization mechanism to give 1-adamantyl carbonium–chloroformate ion pairs which, in solvents of low polarity, can lose carbon dioxide and collapse to 1-adamantyl chloride molecules. In nitrobenzene, and in mixtures with benzene which are rich in nitrobenzene, an increase in the ease of formation of solvent-separated ion pairs or free carbonium ions can lead to an increased development of product derived from alkylation of the solvent. It should be noticed that the bridgehead structure of the 1-adamantyl carbonium ion does not allow backside attack upon a tight ion pair and, in the presence of localized counterionic attraction, solvolysis will require a solvent molecule to intrude between the components of the ion pair; corresponding to solvent separation of the ion pair as a prerequisite for solvolysis.

The feasibility of nitrobenzene alkylation was confirmed by isolation and characterization of 1-(*m*-nitrophenyl)adamantane from a decomposition carried out in the presence of silver hexafluoroantimonate, conditions leading to the precipitation of chloride and replacement by the extremely weakly nucleophilic hexafluoroantimonate ion.[11]

At 54.2°, and with 0.06 *M* solutions, the relative decomposition rates in decane, benzene, and nitrobenzene are as 1:1260:205,000. The decane to nitrobenzene ratio is about 20 times greater than the value reported for α-methylallyl chloroformate—a decomposition which was considered, at least in the more polar solvent, to be an ionic process.[3d] Due to the decomposition rate in decane being sensitive to the initial concentration of chloroformate ester, the magnitude of the ratio will decrease somewhat as the initial concentration of 1-adamantyl chloroformate is increased. The increase in specific rate with increasing concentration of the relatively polar solute is, in itself, indicative of ionic character within the decomposition mechanism, even in a solvent of very low polarity such as decane.

Chloride ion in aprotic solvents is known to bring about SN2-type replacement of chloroformate by chloride.[9] However, SN2 attack is excluded for 1-adamantyl chloroformate, and the modest increase in rate observed upon adding tetra-*n*-butylammonium chloride to a decomposition in nitrobenzene is best explained in terms of a "positive salt effect" upon a unimolecular ionization process. Consistent with this explanation, the rate increase by a factor of 1.68 for a 0.198 *M* addendum at 25.0° is quite similar to the rate increase by a factor of 1.98 on adding 0.200 *M* tetraethylammonium perchlorate to the unimolecular elimination reaction of *t*-butyl chloride in aceonitrile, at 45.0°.[13]

An alternate ionization process, which would also be consistent with the observed solvent dependence of the decomposition rate, involves not an ionization followed by fragmentation of the chloroformate anion, but a synchronous ionization-fragmentation process of the type



$$\underset{\overset{\|}{O}}{\text{ROCCl}} \xrightarrow{\text{slow}} \text{R}^+\cdot\text{CO}_2\cdot\text{Cl}^- \xrightarrow[-\text{CO}_2]{\text{fast}} \text{R}^+\cdot\text{Cl}^- \xrightarrow{\text{fast}} \text{RCl}$$

It was recently suggested[14] that the chloride ion catalyzed decompositions of chloroformates in acetonitrile[9] may possibly involve a replacement-fragmentation process rather than an SN2 process followed by fragmentation of the chloroformate anion and, in view of this suggestion, the possibility of a corresponding ionization-fragmentation process requires careful consideration.

The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, listed in Table II, vary with the solvent composition in a seemingly erratic manner. However, such behavior is known to be a feature of mixed solvent systems.[15] One aspect of the kinetic response to the introduction of *meta* or *para* substituents in the decomposition of α-phenylethyl chloroformates[4] parallels our observations of the effect of varying the solvent composition. In both studies, while the specific rate of decomposition varies in a fairly uniform way with the σ value of the substituent or the percentage composition of the mixed solvent, the entropies and enthalpies of activation appear to be much more complex functions of the appropriate variable.

Of considerable significance is a comparison of the entropies of activation with those expected for four-centered, ion-pair, and ionization-fragmentation processes. Strong support for the ion-pair process comes from the close similarity of the entropy of activation values, −12.0 to −5.7 eu, with the values of −12.0 to −8.0 eu reported for the SN1 solvolyses of 1-adamantyl halides in 80% aqueous ethanol.[16] An ordered four-centered transition state would have been expected to show a somewhat larger negative value; for example, the decomposition of α-phenylethyl chloroglyoxalate was believed to proceed *via* a multicentered

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(11) Dissolving in the more nucleophilic acetonitrile, a solvent with polarity similar to nitrobenzene, led to the formation of a white precipitate with no carbonyl absorption in the infrared. Addition of water, followed by filtration, gave material which analyzed for 59.8% 1-adamantyl chloride and 40.2% N-(1-adamantyl)acetamide. On exposure to the atmosphere, the 1-adamantyl chloride was lost by sublimation and N-(1-adamantyl)acetamide was isolated; mp 149.5–150.5° (lit.[12] 148°). It has not been possible to obtain reproducible analyses for the initial precipitate which reacts as if, at least in part, it possesses the structure: $C_{10}H_{15}N{=}C(Cl)CH_3$, or the ionic equivalent: $(C_{10}H_{15}NCCH_3)^+Cl^-$.

(12) H. Stetter, M. Schwarz, and A. Hirschhorn, *Ber.*, **92**, 1629 (1959).

(13) D. N. Kevill and J. E. Dorsey, *Chem. Ind.* (London), 2174 (1967), and unpublished data.

(14) J. F. King and D. J. H. Smith, *J. Am. Chem. Soc.*, 89, 4803 (1967).

(15) For a discussion, see J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, pp 397–402.

(16) P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, 83 2700 (1961).

transition state on the basis of an entropy of activation of −27 eu.[3f] On the other hand, an ionization-fragmentation process would be expected to have a less negative, or even positive, value; for example, the solvolysis of neopentyl chlorosulfate in 10 *M* aqueous dioxane was postulated to proceed *via* an ionization-fragmentation process largely on the basis of its entropy of activation value.[17]

Nitrobenzene has been used as an inert solvent for studies of Friedel–Crafts alkylation of more reactive aromatics.[18] Alkylation was assumed to occur at an ion-pair or addition-complex stage, and, indeed, the kinetic pattern was inconsistent with attack by free carbonium ions. It is attractive to assume that, in the ionic decomposition of chloroformate esters, alkylation of nitrobenzene can compete with collapse to the alkyl chloride, or to olefin and hydrogen chloride, only when dissociated carbonium ions can serve as the alkylating species. The extent of alkylation by an ion-pair species will be unaffected by addition of chloride ion containing salts and any reduction in the extent of acid production, which accompanies alkylation, will be indicative of competition between solvent and chloride ion for dissociated 1-adamantyl carbonium ions. Further, the correlation between the reduction in the extent of acid production and the concentration of added chloride should be consistent with the simple mathematical form required for such a competition.

In the absence of added chloride salts and excluding the possibility of an extraordinarily large preference for recombination with the minute concentration of simultaneously developed chloride ion, the formation of dissociated 1-adamantyl carbonium ions accompanying the decomposition of 1-adamantyl chloroformate will be followed by solvolysis. Hydrogen chloride produced in the solvolysis will not only contain non-nucleophilic chloride but it will also effectively deactivate other chloride ions present, by complexing to give hydrogen dichloride anions.[19] Under these conditions, the extent of acid formation can, to a good approximation, be used as a measure of the extent of dissociated carbonium ion production. A reduction in the extent of acid production, on addition of tetra-*n*-butylammonium chloride, will indicate a competition between chloride ion and solvent for dissociated 1-adamantyl carbonium ions

$$\mathrm{ROCOCl} \xrightarrow{\text{several steps}} \mathrm{R^+} + \mathrm{Cl^-} + \mathrm{CO_2}$$

$$\mathrm{R^+} \begin{cases} \xrightarrow[k_2{}^{1}]{\mathrm{Cl^-}} \mathrm{RCl} \\ \xrightarrow[k_2{}^{11}]{\mathrm{C_6H_5NO_2}} \mathrm{RC_6H_4NO_2} + \mathrm{H^+} \end{cases}$$

and for the product formation from *dissociated* carbonium ions

$$\frac{[\mathrm{RCl}]}{[\mathrm{RC_6H_4NO_2}]} = \frac{k_2{}^{1}[\mathrm{Cl^-}]}{k_2{}^{11}[\mathrm{C_6H_5NO_2}]} = \alpha[\mathrm{Cl^-}]$$

where α represents $k_2{}^1/k_2{}^{11}[\mathrm{C_6H_5NO_2}]$, and $\alpha = [\mathrm{RCl}]/[\mathrm{acid}][\mathrm{Cl^-}]$ or α = (% acid in absence of *n*-$\mathrm{Bu_4NCl}$ − % acid in presence of *n*-$\mathrm{Bu_4NCl}$)/(% acid in presence of *n*-$\mathrm{Bu_4NCl}$)[*n*-$\mathrm{Bu_4NCl}$].

Several values of α calculated at 15.0°, using the data of Table VI, are given in Table VII. The reasonably constant α values obtained from the treatment give good support to the hypothesis that acid production, in the absence of added chloride salts, can be equated to production of dissociated 1-adamantyl carbonium ions.

Table VII. Determination of α on Addition of *n*-$\mathrm{Bu_4NCl}$ to the Reaction of 0.093 *M* 1-Adamantyl Chloroformate in Nitrobenzene at 15.0°

10^3[*n*-$\mathrm{Bu_4NCl}$], *M*	2.58	5.16	7.74	23.2
α[a]	44	32	38	25

[a] Calculated from data in Table VI. Assuming nitrobenzene to be 16.1 *M* and taking a value for α of 34, the competition factor between chloride ions and nitrobenzene molecules, for dissociated 1-adamantyl carbonium ions, ($k_2{}^1/k_2{}^{11}$) is 550.

The acid production in toluene (1.9% at 64.7°) is comparable to that in nitrobenzene, and about four times as large as in benzene, at this temperature. As mentioned previously, for Friedel–Crafts reactions using nitrobenzene as solvent, more reactive aromatics, such as toluene, are alkylated by an ion-pair (or earlier) stage.[18] It is reasonable to assume that, in toluene, alkylation can compete with collapse of 1-adamantyl chloride ion pairs and, also, that alkylation will be more pronounced than for the unactivated benzene.

Experimental Section

Purification of Materials. Benzene (J. T. Baker "Analyzed") and toluene (J. T. Baker "Analyzed") were refluxed over molten potassium and distilled. Decane (Aldrich) was purified by distillation. Tetra-*n*-butylammonium chloride (Eastman) was recrystallized from acetone and dried under vacuum at 70° for 24 hr.

A 3-l. portion of nitrobenzene (J. T. Baker "Analyzed") was treated by the following washing procedures: (1) washed twice with 1 l. of 1 *N* sulfuric acid, followed by a 2-l. water wash; (2) washed twice with 1 l. of 1 *N* sodium hydroxide, followed by a 2-l. water wash; (3) washed twice with 1 l. of 1 *N* sulfuric acid, followed by a 2-l. water wash; (4) washed once with 2 l. of saturated sodium carbonate solution, followed by a 2-l. water wash. The resulting nitrobenzene was dried by vigorous stirring with calcium chloride. Slow distillation at reduced pressure was followed by fractional freezing. The final volume was about 2.5 l.

1-Adamantyl Chloroformate. To 240 ml of a 12.5% solution of phosgene in benzene (Matheson Coleman and Bell) at 0–5° was added a solution of 8.0 g of 1-adamantanol and 7.0 g of pyridine in 200 ml of benzene, over a period of 1 hr and with vigorous stirring. The reaction solution was allowed to stand for 1 hr at room temperature after which it was extracted with two 500-ml portions of ice water and dried with anhydrous sodium sulfate, followed by evaporation to dryness at room temperature. The residue was recrystallized once from 30 ml of a 50:50 (v/v) mixture of *n*-hexane and *n*-pentane at −20° (ice–salt bath), quickly filtered, and dried under reduced pressure. Obtained was 6.8 g (60.3% yield) of a white, crystalline solid: mp (sealed tube) 50–51° dec (lit.[8] 45–46°); the infrared spectrum, KBr pellet, includes $\lambda_{\max}$ 3.45, 3.52 (s), 5.60 (s) (C=O), 8.73 (s and broad) (C—O), 12.04, 12.51 (s), and 14.55 (s and sharp) (C—Cl) μ.

Anal. Calcd for $\mathrm{C_{11}H_{15}O_2Cl}$: Cl, 16.51. Found: Cl, 16.41.

A sample of 1-adamantyl chloroformate will hydrolyze upon continued contact with humid air. Storage in an evacuated desiccator over $\mathrm{CaCl_2}$, at about 0° (cold room), was sufficient to keep the chloroformate essentially unchanged for at least 2 weeks. Repeated melting raised the melting point to 163–165°, corresponding to that for 1-adamantyl chloride (lit.[12] 165°).

1-(*m*-Nitrophenyl)adamantane. A solution of 1.20 g (0.0035 mol) of silver hexafluoroantimonate in 25 ml of nitrobenzene was added, at room temperature, to 0.75 g (0.0035 mol) of 1-adamantyl chloroformate. The nitrobenzene solution was filtered from precipitated silver chloride, added to 50 ml of diethyl ether, and washed

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[17] E. Buncel and J. P. Millington, *Can. J. Chem.*, **43**, 556 (1965).

[18] H. C. Brown and M. Grayson, *J. Am. Chem. Soc.*, **75**, 6285 (1953).

[19] Y. Pocker, *J. Chem. Soc.*, 240 (1958).

Table VIII

A. Temperature, 54.2°; 2-ml Aliquots; $[C_{10}H_{15}OCOCl]$ = 0.0620 *M*; Solvent, 100% $C_6H_5NO_2$;
Titers in Milliliters of 0.00984 *M* Methanolic NaOMe

Time, sec	0	35	70	105	130	160	195	275	345
Titer	5.66	3.27	2.45	1.47	1.36	1.00	0.50	0.42	0.18
10^2k_1, sec^{-1}		(1.57)	1.19	1.28	1.09	1.08	1.24	0.96	1.00

B. Temperature, 54.2°; 2-ml Aliquots; $[C_{10}H_{15}OCOCl]$ = 0.0624 *M*; Solvent, $C_6H_5NO_2$–C_6H_6 (20:80);
Titers in Mililliters of 0.00979 *M* Methanolic NaOMe

Time, sec	0	55	240	425	595	795	1020	1290	1600	2000
Titer	9.22	8.95	8.07	7.18	6.79	6.14	5.10	4.40	3.84	2.91
10^4k_1, sec^{-1}		5.41	5.55	5.87	5.14	5.12	5.81	5.73	5.47	5.76

C. Temperature, 54.2°; 2-ml Aliquots; $[C_{10}H_{15}OCOCl]$ = 0.0622 *M*; Solvent, 100% C_6H_6;
Titers in Milliliters of 0.00984 *M* Methanolic NaOMe

10^3 time, sec	0	2.64	3.54	4.26	5.40	6.06	7.08	8.04	9.12
Titer	9.13	7.79	7.25	6.99	6.49	6.19	5.82	5.41	5.06
10^5k_1, sec^{-1}		6.01	6.51	6.28	6.32	6.42	6.39	6.51	6.47
10^3 time, sec	10.02	10.86	12.36	13.68	15.18	16.14	17.46	18.96	
Titer	4.80	4.54	4.11	3.76	3.44	3.19	2.91	2.70	
10^5k_1, sec^{-1}	6.42	6.43	6.46	6.48	6.44	6.52	6.56	6.43	

D. Temperature, 0.0°; 2-ml Aliquots; $[C_{10}H_{15}OCOCl]$ = 0.0618 *M*; Solvent, $C_6H_5NO_2$–C_6H_6 (60:40);
Titers in Milliliters of 0.00979 *M* Methanolic NaOMe

10^3 time, sec	0	14.5	17.9	23.9	34.3	43.4	53.5	72.2	92.9
Titer	8.67	7.97	7.78	7.44	6.99	6.62	6.27	5.62	4.82
10^6k_1, sec^{-1}		5.80	6.06	6.41	6.35	6.21	6.06	6.00	6.32

with water until the washings were neutral to litmus. The organic layer was dried over anhydrous Na_2SO_4, and the volume was reduced to 5 ml by distillation. The 5-ml residue was added to an 18-in. alumina column and eluted with hexane. Evaporation of the effluent gave 90 mg of an off-white solid, mp 60–80°. Recrystallization from methanol gave 35 mg (4% yield) of a white solid, mp 86–87.5°; infrared spectrum included λ_{max} 3.26, 3.47 (s), 3.52, 6.78, 6.96, 7.50 (s and sharp), 7.70, 12.00, 12.53 (sharp), 3.61 (s and sharp), 13.83, 14.69 (s and sharp), and 14.90 μ; the pmr spectrum showed a complex multiplet between τ 1.7 and 2.6 (4 aromatic protons) and signals accounting for 15 aliphatic protons between τ 7.7 and 8.3.

Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.60; H, 7.45; N, 5.37.

Other isolation techniques gave higher yields, but reduced purity. Since our purpose (to show that 1-adamantyl carbonium ions can interact with nitrobenzene) was achieved, we did not attempt to improve upon the rather low yield obtained by the above procedure.

Product Study in Benzene. A solution of 0.537 g of 1-adamantyl chloroformate in 25 ml of benzene was allowed to react, at 54.2°, for 115 hr. Evaporation to dryness gave 0.401 g (94% yield) of white crystals of 1-adamantyl chloride, mp 163–165° (lit.[12] 165°); the infrared spectrum was identical with that of an authentic sample, prepared as described previously.[12] Refluxing 0.2564 g with silver nitrate in aqueous ethanol for 12 hr, gave 0.2093 g of AgCl, 97.3% of the theoretical amount as calculated for $C_{10}H_{15}Cl$.

Kinetic Procedures. For the slower runs, a bulk solution of 1-adamantyl chloroformate was subdivided and each subdivision placed in an appropriate constant temperature bath. After a short pause for temperature equilibration, two zero points were taken from each subdivision and subsequent aliquots were removed at suitable time intervals. Each point consisted of a 2-ml, aliquot, removed by pipet from the bulk solution and, after hydrolysis of unreacted chloroformate ester in 20 ml of 70% aqueous acetone, titrated with 0.01 *M* sodium methoxide in methanol to a resorcinol blue end point. For runs in decane, in order to preserve homogeneity, hydrolysis was carried out in 85% aqueous acetone.

For runs too fast to follow by the above technique, the requisite weight of 1-adamantyl chloroformate was weighed directly into a 25-ml flask. A 25-ml portion of temperature-equilibrated solvent was then added to the chloroformate. After vigorous shaking, the run was carried out as before, but with only one zero point for very fast runs. Mixed solvents were prepared on a weight percentage basis.

The first-order rate coefficients reported within Table I were obtained from a statistical computation of the slope of a plot of log $(\text{titer})_{t=t}$ against time. In the four illustrative runs which appear in Table VIII, the first-order rate coefficients reported for each point are the integrated first-order rate coefficients with respect to the 1-adamantyl chloroformate.

Acid Production Accompanying Decomposition. All solvents used in acid production determinations were dried immediately before use by repeated passage through an 18-in. column of Linde 4A Molecular Sieves. A 5-ml portion of temperature-equilibrated solvent was added to 0.100 g of 1-adamantyl chloroformate contained within a dry 10-ml flask (to give a 0.093 *M* solution), and the flask was tightly stoppered. For determinations with added tetra-*n*-butylammonium chloride, the salt was introduced into the solvent, prior to the addition to the 1-adamantyl chloroformate, by appropriate dilution of a concentrated stock solution.

After at least ten half-lives, three 1.00-ml aliquots were removed and each was drowned in 30 ml of 70% aqueous acetone. The acid produced was titrated against a standard methanolic solution of sodium methoxide, using resorcinol blue as indicator.