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Kinetic Study of the Nitrolysis of Haloadamantanes

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Abstract—The kinetics of nitrolysis of haloadamantanes containing halogen atoms in the bridging and bridgehead positions with fuming nitric acid have been studied. The effective nitrolysis constants of eight haloadamantane derivatives have been determined. The reaction is described by pseudo-first-order kinetic equation, and the reactivity decreases as the number of halogen atoms in the substrate molecule increases. Haloadamantanes with less electronegative halogens show higher reactivity.

Keywords: kinetics, haloadamantanes, nitrolysis, mechanism, fuming nitric acid, reactivity

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Polyfunctional adamantane derivatives are key starting materials in the synthesis of biologically active compounds and advanced materials [1–5]. Among them, polyhalogenated adamantanes are most synthetically accessible. For example, 1,3-dibromoadamantane is used as a molecular scaffold in the design of metal–organic frameworks [6] and polymeric materials [7, 8] and synthesis of biologically active compounds [9–11] and alkylboronic acid esters for cross-coupling reactions and medicinal chemistry [12, 13]. 1,3-Dibromoadamantane was reported to undergo transformations accompanied by change of the molecular skeleton [14–17]. The synthetic potential of 1,3-dichloro- and 1,3-difluoroadamantanes has been explored to a lesser extent [18, 19]. 1,3,5-Tribromoadamantane is the basic structural unit of tripod systems [20, 21] and is used to obtain other polyfunctionalized adamantane derivatives [22].

Until present, nucleophilic substitution in the haloadamantane series [23–29] and anodic oxidation of these compounds [30–33] have been well documented. On the other hand, only a few data are available on reactions of haloadamantanes involving oxidative cleavage of the C–Hlg bond [34]. In continuation of our studies on the mechanisms of oxidation of cage substrates [35–37], herein we report some kinetic data for the nitrolysis of polyhaloadamantanes.

The nitrolysis of haloalkanes with nitric acid was studied in [38]. It was presumed that heterolytic dissociation of the C–Hlg bond in nitric acid gives the corresponding carbocation which is then stabilized by nitrate ion to form alkyl nitrate as a final product. Treatment of 1-haloadamantanes with fuming nitric acid was reported to afford adamantan-1-yl nitrate and adamantane-1,3-diyl dinitrate [39]; in the reaction of 2-haloadamantanes with nitric acid, the nytrolysis of the C–Hlg bond was accompanied by oxidation to adamantan-2-one [40].

Cleavage of the C–Hlg bond is likely to involve one-electron transfer with the formation of adamantyl radical cation which then decomposes to adamantyl cation and halogen atom. This was confirmed by photoelectron spectra of a number of 1-haloadamantanes. The adiabatic ionization potentials were estimated at 9.63 eV for 1-bromoadamantane [41], 9.30 eV for 1-chloroadamantane [42], and 8.79 eV of 1-iodoadamantane [41].

In order to elucidate mechanistic details of the C–Hlg bond heterolysis in haloadamantanes, in this work we studied the kinetics of nitrolysis of haloadamantanes containing halogen atoms in the bridging and bridgehead positions in the system nitric acid–methylene chloride. The substrates were 1-fluoroadamantane (**1**), 1,3-difluoroadamantane (**2**), 1,3-dichloroadamantane (**3**), 1,3-dibromoadamantane (**4**), 2,2-dichloroadamantane (**5**), 2,2-difluoroadamantane (**6**), 1,3,5-tribromoadamantane (**7**), and methyl 3-chloroadamantane-1-carboxylate (**8**).

The kinetic measurements were carried out using 100% nitric acid in methylene chloride. The reaction

Table 1. Orders of the reaction of 1-fluoroadamantane (**1**)[a] with nitric acid in adamantane substrate

$[HNO_3]$, M	Reaction order
0.75	0
1.00	0.11
1.50	0.62
1.75	0.91
2.00	[b]

[a] $c_0 = 0.025–0.05$ M, 20°C.

[b] The initial reaction rate exceeded 8×10^{-3} mol/s, so that the error in the determination of the reaction order was very large.

mixtures were analyzed by GLC using 1,4-dinitrobenzene as internal standard. The reactions were run at 20°C, the initial substrate concentration was $c_0 = 0.025$ M, and the concentration of nitric acid was varied from 4 to 8 M. Before GLC analysis, the reaction mixtures were quenched by pouring onto crushed ice.

On the basis of generally accepted theoretical views and published data [38], the following reactivity order of adamantyl halides toward nitrolysis can be expected: I > Br > Cl > F. The relative rates of the reactions of 1-haloadamantanes with nitronium salts in acetonitrile were determined (competitive reaction method) as F:Cl:Br:I = 1:6.6:67:240 [43]. The reaction is strongly exothermic; for instance, the heat effect in the nitrolysis of *tert*-butyl chloride with nitric acid (1:1, by weight) was 80 kJ/mol [44].

Unlike the data of [43], 1-fluoroadamantane (**1**) turned out to be at least 3 orders of magnitude more reactive than unsubstituted adamantane in the reaction with nitric acid [35]. The conversion of 1-fluoroadamantane (**1**, 0.05 M) at –10°C in a mixture of HNO_3 (4 M) and CH_2Cl_2 was complete even in 30 s.

Table 2. Rate constants for the nitrolysis of haloadamantanes **2**–**8**[a]

Substrate (no.)	$[HNO_3]_0$, M	k_{eff}, s^{-1}
2,2-Dichloroadamantane (**5**)	4	$5.61\pm0.13\times10^{-3}$
2,2-Difluoroadamantane (**6**)	4	$0.15\pm0.05\times10^{-3}$
1,3-Dibromoadamantane (**4**)	4	$5.92\pm0.73\times10^{-3}$
1,3-Dichloroadamantane (**3**)	4	$0.72\pm0.11\times10^{-3}$
1,3-Difluoroadamantane (**2**)	4	$0.64\pm0.11\times10^{-3}$
1,3-Difluoroadamantane (**2**)	5	$1.62\pm0.20\times10^{-3}$
1,3-Difluoroadamantane (**2**)	6	$3.47\pm0.48\times10^{-3}$
1,3-Difluoroadamantane (**2**)	7	$3.72\pm0.47\times10^{-3}$
1,3-Difluoroadamantane (**2**)	8	$4.50\pm0.71\times10^{-3}$
1,3,5-Tribromoadamantane (**7**)	4	$1.94\pm0.21\times10^{-3}$
Methyl 3-chloroadamantane-1-carboxylate (**8**)	4	$1.26\pm0.13\times10^{-3}$

[a] $c_0 = 0.025$ M, CH_2Cl_2, 20°C.

The order of the reaction in the substrate was determined from the initial rates of nitrolysis of 1-fluoroadamantane (**1**) as a model (Table 1). It was found that, as the concentration of nitric acid increases, the reaction order changes from zero to a fractional value which then approaches unity. Such change of the reaction order from first to zero is also typical of nitroxylation [35] and nitration in inert solvents [45] and is related to change of the limiting step. At low nitric acid concentrations, the overall rate of nitrolysis of reactive substrates depends on the rate of formation of nitronium cation in the reaction system.

Obviously, change to the first order in substrate is possible when the reactivity of the latter decreases, which can be achieved by introduction of additional electron-withdrawing substituents into haloadamantane molecule. In fact, the nitrolysis of polyhaloadamantanes **3**–**8** and methyl 3-chloroadamantane-1-carboxylate (**2**) is described by pseudo-first-order kinetic equation:

$$\frac{\partial c}{\partial \tau} = k_{\mathrm{eff}}[c], \text{ where } k_{\mathrm{eff}} = k[\mathrm{HNO_3}]_n.$$

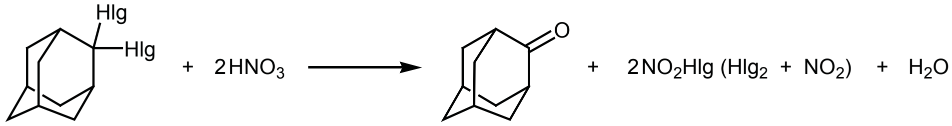
Figure 1 shows semilog kinetic curves for the nitrolysis of polyhaloadamantanes. The observed linear dependences suggest first order of the reaction in the adamantane substrate. The effective rate constants for the nitrolysis of haloadamantanes **2**–**8** are given in Table 2. Comparison of the rate constants for the nitrolysis of methyl 3-chloroadamantane-1-carboxylate (**8**) and nitroxylation of methyl adamantane-1-carboxylate $\{k_{eff} = (3.9\pm0.4)\times10^{-6}\ s^{-1}$ [35]$\}$ makes it possible to roughly estimate the rates of dissociation of tertiary C_{Ad}–Cl and C_{Ad}–H bonds by the action of nitric acid. The ratio of these rate constants is 325:1. It should be noted that this value was obtained assuming equal effects of the methoxycarbonyl group on the rates of nitrolysis and nitroxylation, since analogous ratio for unsubstituted adamantane is considerably higher. The rate of nitrolysis of 1-chloroadamantane was so high that even its approximate estimation was impossible.

The reactivity increases in the series 1,3-difluoroadamantane (**2**) < 1,3-dichloroadamantane (**3**) < 1,3-dibromoadamantane (**4**), and the difference in the nitrolysis rate constants of dihaloadamantanes **2** and **3** does not exceed the experimental error, whereas dibromide

Scheme 1.

$$R{-}Hlg + 2HNO_3 \longrightarrow R{-}ONO_2 + 1/2Hlg_2 + NO_2 + H_2O$$

Scheme 2.



4 is more reactive by approximately an order of magnitude. The rate of nitrolysis of 1,3,5-tribromoadamantane (**7**) is only three times lower than that found for dibromide **4**. Such small differences in the reactivity can be explained assuming that polar substituent effects insignificantly influence the transition state which occupies different positions on the reaction coordinate for fluoro, chloro, and bromo derivatives. Moreover, it is quite probable that the nitrolysis of different adamantyl halides follows different mechanisms [46], though it can be described by a common formal scheme reflecting its stoichiometry (Scheme 1).

The given equation, according to which oxidation of $Hlg^{\cdot}$ to Hlg_2 is a necessary condition for nitrolysis, is inapplicable to the substitution reaction of fluoro derivatives. The redox potential of nitronium cation (1.6–1.9 V) is insufficient to oxidize fluoride anion to fluorine [$F^-/(1/2F_2)_g$ 2.87 V] [47]. Furthermore, fluorine itself oxidizes nitric acid and nitric anhydride to give nitryl fluoride [48].

A different reactivity order was observed in the nitrolysis of 2,2-dihaloadamantanes which is outlined in Scheme 2. The reaction with 2,2-difluoroadamantane (**6**) is 37 times slower than with 2,2-dichloroadamantane (**5**) and 4 times slower than with 1,3-difluoroadamantane (**2**). On the other hand, the rate constant of nitrolysis of geminal dichloride **5** is 8 times higher than that of 1,3-dichloro isomer **3**. In this case, two opposite effects are operative: negative inductive effect of the geminal halogen atom destabilizes the transition state, whereas the stability of intermediate halocarbenium ion increases due to *n*–2*p* resonance interaction [49]. Unlike solvolytic reactions, geminal halogens reduce the rate of nitrolysis [46], i.e., the inhibitory inductive effect is stronger than conjugation effect, especially in the case of difluoride **6**.

The order of the reaction in nitric acid (n) can be determined from the slope of the kinetic curves in the coordinates $\log k_{\mathrm{eff}}$—$\log[\mathrm{HNO_3}]$ using the equation

$$\log k_{\mathrm{eff}} = \log k + n \log[\mathrm{HNO_3}].$$

Figure 2 shows the dependence of rate of nitrolysis of difluoride **2** on the concentration of nitric acid. The slope is equal to 2.81. Taking into account fairly high dispersion of the experimental data, the nitrolysis order in nitric acid can be assumed to be equal to 3. It should be noted that formally fifth order in nitric acid was found for the nitroxylation reaction [35]. This value surprisingly accurately coincides with the order in nitric acid found by studying the kinetics of nitration of alkylbenzenes in carbon tetrachloride [50]. High reaction orders in nitric acid for the nitration in inert solvents are likely to be general. For example, the

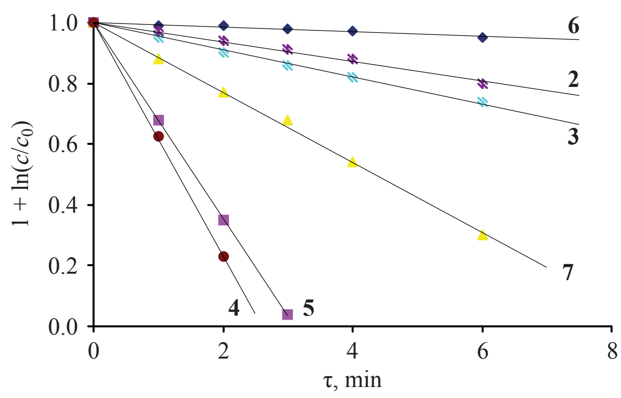


Fig. 1. Semilog kinetic curves for the nitrolysis of haloadamantanes **2**–**7**; c_0 = 0.025 M, $[\mathrm{HNO_3}]_0$ = 4 M, CH_2Cl_2, 20°C.

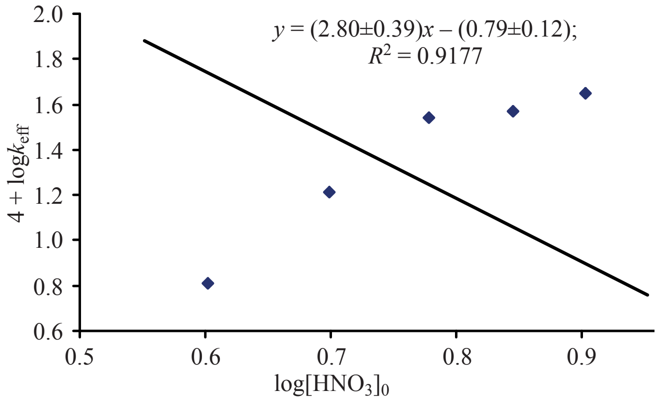
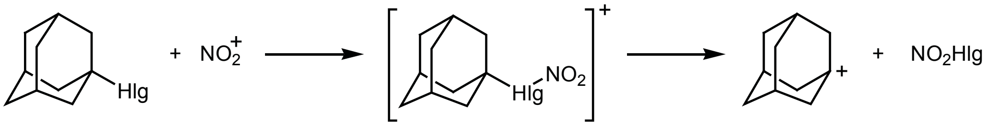
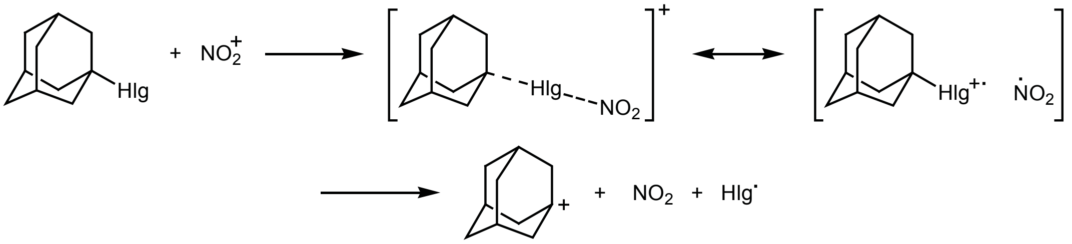


Fig. 2. Log plot of the effective rate constant for the nitrolysis of 1,3-difluoroadamantane (**2**) versus nitric acid concentration; CH_2Cl_2, 20°C, c_0 = 0.025 M.

Scheme 3.



Scheme 4.



nitration of oxiranes in methylene chloride is characterized by third order in nitric acid and second order in nitric anhydride [51]. The rate of nitration of cellulose in methylene chloride is also proportional to the concentration of nitric acid at a power of 3 (calculated from the data of [52]). It is attractive to suppose that the high order in nitric acid is not related to solvent effect but is intrinsic to the reaction itself. This assumption is indirectly supported by the kinetic study of nitration of aromatic substrates with a solution of nitric anhydride in nitric acid [53], which showed that the reaction rate increases to a greater extent than the concentration of nitronium cation in the system. These findings are likely to reflect oligomeric nature of fuming nitric acid [54] and the existence of solvation species and ion–molecular equilibria whose nature has not been clearly understood [54–56].

Analysis of our kinetic data for the reactions of haloadamantanes with nitric acid suggests that several nitrolysis mechanisms are possible and that the reaction under study is a particular case of oxidative substitution at a saturated carbon atom [46]. One of the possible reaction paths is shown in Scheme 3, according to which one-electron oxidation of adamantyl halide with nitronium ion gives intermediate halonium ion, and the latter decomposes to nitryl halide and adamantyl cation whose stabilization with a nucleophilic species yields final products.

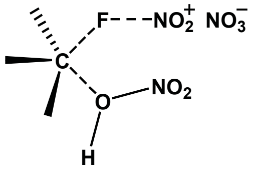


Fig. 3. Postulated transition state for the nitrolysis of 2,2-difluoroadamantane.

We believe that somewhat different reaction scheme is more probable (Scheme 4). Herein, the transition state is a superposition of halonium ion and radical pair formed by haloadamantane radical cation and nitrogen dioxide, and the primary intermediate is adamantyl cation. As applied to 2,2-dihaloadamantanes, the intermediate is halocarbenium ion which is converted to unstable geminal halo nitrate, and the latter decomposes to adamantan-2-one and nitryl halide.

In the case of nitrolysis of adamantyl fluorides for which the formation of halonium ions is hardly probable, a concerted mechanism could not be ruled out. Dissociation of the C–F bond is likely to be accompanied by synchronous formation of C–O bond in the protonated form of final nitric acid ester due to participation of solvation shell of nitronium cation (Fig. 3).

Figure 4 shows the reactivity series of haloadamantane derivatives in the nitrolysis in the system HNO_3–CH_2Cl_2, which was inferred from the results of our study.

EXPERIMENTAL

Quantitative analysis of the reaction mixtures was performed with a Thermo Scientific Focus gas chromatograph (USA) equipped with a 0.5-m×3-mm column packed with 5% SE-30–3% CKTFT-100 on Inerton AW-HMDS (0.20–0.25 mm); oven temperature programming from 80 to 120°C at a rate of 5 deg/min; injector temperature 120°C; carrier gas helium. The melting points were measured in capillaries on an MPM-H2 melting point apparatus (Germany) and are uncorrected. Compounds **1**, **3**, and **7** with a purity of ≥95.0% were provided by A.M. Aleksandrov (Kukhar' Institute of Bioorganic and Petroleum Chemistry, National Academy of Sciences of Ukraine). 1,3-Dibromoadamantane (**5**) [6], 1,3,5-tribromoada-

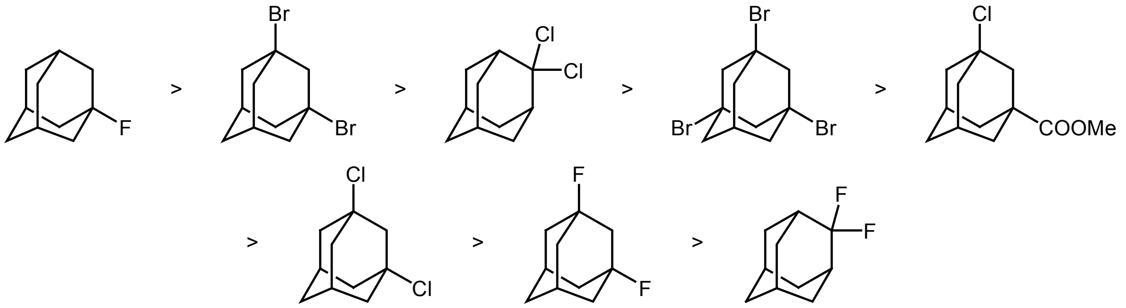


Fig. 4. Reactivity series of haloadamantane derivatives in the nitrolysis with nitric acid in methylene chloride at 20°C.

mantane (**8**) [57], and 2,2-dichloroadamantane (**4**) [58] were synthesized according to reported procedures.

3-Chloroadamantane-1-carboxylic acid. 1-Chloroadamantane (**1**), 3 g (0.022 mol), was added with cooling to 15 mL (0.36 mol) of 98% nitric acid, and the mixture was kept for 1 h at a temperature not exceeding 20°C. The mixture was treated with 10 mL of concentrated aqueous HCl, kept for 1 h at 20°C, and poured onto ice, and the precipitate was filtered off. Yield 27%, mp 147–148°C [59].

Methyl 3-chloroadamantane-1-carboxylate (2) was synthesized from 3-chloroadamantane-1-carboxylate as described in [60].

Kinetic measurements. The reaction of haloadamantanes **1**–**8** with nitric acid in methylene chloride was carried out in a glass reactor equipped with a stirrer, thermometer, and sampler, which was maintained at a constant temperature within ±0.5°C. Nitric acid (100%, $d = 1.522$ g/cm^3) was distilled under reduced pressure (20 torr) just before use. Methylene chloride was purified by standard method [61]. Components of the reaction mixtures were quantitated by the internal standard method [62] using 1,4-dinitrobenzene as internal standard. The reactor was charged with a solution of haloadamantane **1**–**8** in 5 mL of anhydrous methylene chloride, the solution was adjusted to a required temperature, and a solution of 100% nitric acid in methylene chloride was added over a period of 2 s at that temperature (the overall volume of the mixture was 20 mL). Samples (2 mL each) were withdrawn at definite time intervals, mixed with 10 mL of ice water, and neutralized with sodium carbonate. The organic phase was separated using a separatory funnel, dried over sodium carbonate, and analyzed by GLC. Each experiment was carried out in triplicate, and the rate constants were calculated as a mean of *n* values. The order of the reaction with respect to the substrate was determined from the initial rates at different initial concentrations [63].

CONCLUSIONS

Heterolysis of the C–Hlg bond in haloadamantanes containing halogen atoms in the bridgehead positions involves one-electron transfer with intermediate formation of a radical pair of haloadamantane radical cation and nitrogen dioxide, which decomposes to adamantyl cation with liberation of halogen and NO_2. Adamantyl cation is stabilized via addition of nucleophilic species prevailing in the reaction system.

The nitrolysis of 2,2-dihaloadamantanes initially gives intermediate halocarbenium ion which is converted to unstable geminal halo nitroxy compound, and the latter decomposes to adamantan-2-one and nitryl halide.

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CONFLICT OF INTEREST

The authors declare the absence of conflict of interest.

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