BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (5), 1565—1566 (1978)

Solvolysis in Carboxamides. III.[1)] Solvolysis Rates of 1-Adamantyl Bromide and Tosylate, 2-Adamantyl Tosylate, and *t*-Butyl Chloride in Carboxamides

Seiki Saito, Kenji Doihara, Toshio Moriwake, and Kunio Okamoto*
Department of Synthetics Chemistry, School of Engineering,
Okayama University, Tsushima, Okayama 700
**Department of Hydrocarbon Chemistry, Faculty of Engineering*
Kyoto University, Sakyo-ku, Kyoto 606

(Received June 24, 1977)

Synopsis. Rate constants for the solvolysis of 1-adamantyl bromide and tosylate, 2-adamantyl tosylate, and *t*-butyl chloride in the four carboxamide solvents, *i. e.*, *N,N*-dimethylacetamide, *N,N*-dimethylformamide, *N*-methylacetamide, and *N*-methylformamide, have been determined. The role of the carboxamides as solvolytic solvents has been discussed on the basis of linear free-energy relationship.

Although carboxamides, such as *N,N*-dimethylacetamide (DMA), *N,N*-dimethylformamide (DMF), *N*-methylacetamide (NMA), and *N*-methylformamide (NMF), are expected to be particularly effective solvents for S_N1 solvolyses because of their highly polar characteristics,[2)] little has been studied on the solvolytic feature of these solvents.[1,3)]

It has been commonly accepted that the rate of solvolysis of the adamantyl system reflects the rate of the ionization process, because, for this system, neither rate-determining elimination nor solvation at the rear side of a leaving group is possible. Thus, in the assessment of the ionizing power of solvolytic solvents, the adamantyl system, including 1-adamantyl bromide[4)] (**1**) and tosylate[4b,5)] (**2**), and 2-adamantyl tosylate[6)] (**3**) has been used as the reference compound. In the present paper we wish to report on the ionizing powers of the carboxamides, *i.e.*, DMA, DMF, NMA, and NMF, by the use of above mentioned tertiary systems **1** and **2**, **3**, and *t*-butyl chloride (**4**).

Results and Discussion

The first-order rate constants for the solvolysis of **1**, **2**, **3**, and **4** in the carboxamide solvents are shown in Table 1 along with the Y and m values.[7)] A linear relation between log k_1 and Y has been observed for the carboxamide solvolysis of **1**, **2**, and **3**, and another linear relation has also been observed for many other solvents, including carboxamides, with a range of solvolytic reactivities varying over 8 (for **1**), 5 (for **2**), and 6 (for **3**) powers of ten, excluding the points for carboxylic acids[5,6c,6d)] for **2** and **3**, aqueous trifluoroethanols[4a,6e)] for **1** and **3**, and phenolic solvents[4b)] for **1** and **2**. The correlation coefficients for the latter m-Y relation are 0.996, 0.990, and 0.998, respectively for **1**, **2**, and **3**. On the basis of these linear free-energy relationships, it is expected that the four carboxamide solvents would cause the solvolytic ionization even in the solvolyses of a secondary system,[8)] though their ionizing powers are comparatively low (−1.51— −4.28 as measured by Y-values).

The importance of the nature of a leaving group is demonstrated when the correaltion between the rates for **1** and **2** in several groups of solvents is examined (Fig. 1). The data for the different solvent systems are clearly represented by five lines in Fig. 1. A similar type of dispersion has been found by Harris *et al.*[4c)] in the plots of the log k_1 for **4** against log k_1 for **1** in aqueous ethanols and aqueous trifluoroethanols, and they have suggested that this dispersion is a diagnostic for nucleophilic solvent assistance.[6c)] Our findings for the adamantyl systems, in which nucleophilic solvent assistance[6c)] is prohibited, suggest that, besides the factor pointed out by Harris *et al.*,[4c)] the non-electrostatic contribution (*i. e.*, hydrogen-bonding to the leaving group)[4c)] to the ionization is important and different from a group of solvents to

Table 1. First-order rate constants (k_1)[a)] for the solvolysis of adamantyl compounds and *t*-butyl chloride at 25 °C and the correlation between log k_1 (adamantyl) and Y[b)]

Amide	$k_1/(10^{-5}\ s^{-1})$				Y
	t-BuCl	1-AdBr	1-AdOTs	2-AdOTs	
DMA	4.87×10^{-5}	3.81×10^{-8} [c)]	4.15×10^{-3}	2.91×10^{-7}	−4.28
DMF	2.40×10^{-4}	4.23×10^{-7}	2.89×10^{-2}	1.54×10^{-6}	−3.59[d)]
NMA	4.73×10^{-3}	3.03×10^{-5}	8.25×10^{-1}	2.67×10^{-5}	−2.29
NMF	2.87×10^{-2}	5.23×10^{-4}	8.03	1.78×10^{-4}	−1.51
m (Amides)[e)]	1.00	1.48	1.18	0.997	
m (Solvents)[f)]	1.00	1.27	1.15	0.874	

a) Extrapolated from data at other temperatures (33—145 °C), except for the run, 1-AdOTs in NMF. b) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963). c) Calculated from the plot of log k_1 *vs.* Y. d) The reported values:[3b)] −3.47. e) The m values of the substrates calculated merely for the carboxamides. f) The m values for k_1's respectively in 22, 17, and 12 solvents, including the carboxamides; for k_1's in hydroxylic solvents, see Refs. 4a, 5, 6c—e, and J. M. Harris, A. A. Becker, J. F. Fagan, and F. A. Walden, *J. Am. Chem. Soc.*, **94**, 4484 (1974).

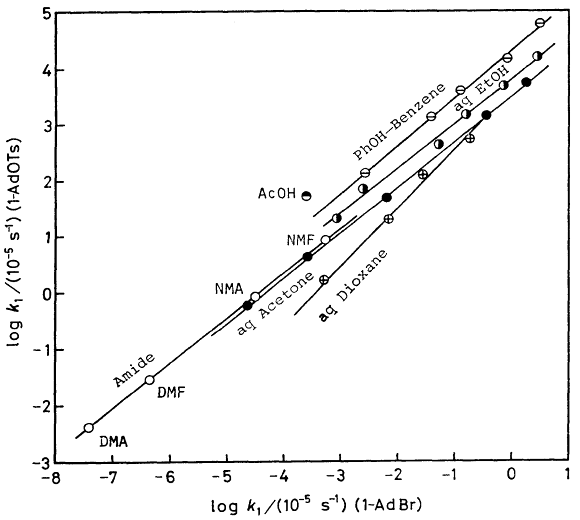

Fig. 1. Correlation of the rates of 1-AdOTs with that of 1-AdBr at 25 °C in different groups of solvents; from Table 1 and Refs. 4a, 4b, and 5.

another, though the definite conclusion is to be expected in a future work.

Experimental

Substrates and Solvents. 1-Adamantyl bromide, mp 119—120 °C (lit[9] mp 119—120 °C), 1-adamantyl tosylate, mp 79—83 °C (lit[10] mp 78—83 °C), and 2-adamantyl tosylate, mp 82.3—83 °C (lit,[6e] mp 82.1—83.4 °C) were prepared following the published methods.[5,11] *t*-Butyl chloride (commercial) was dried ($CaCl_2$) and distilled immediately before use. The four carboxamides were purified by the method described in a previous paper.[1]

Kinetic Measurements. Rates of solvolysis of the tosylates **2** and **3**, and the halides **1** and **4** were respectively determined by an acid-base titration (KOH in EtOH, Thymol Blue–phenolphthalein mixed indicator) and by haldie ion titration (the Volhard method[12]), employing the usual sealed-ampoule technique. As to the run for the tosylates, an acid-catalyzed hydrolysis of the carboxamides due to water contained in the solvent even after rigorous purification, has made an experimental infinity titer greater than the theoretical one. After appropriate correction for the above difference, a good first-order behavior was observed for all kinetic runs over two to three half-lives both in the absence and presence of added pyridine, except for the solvolysis of **2** in DMA at higher temperatures in which the first-order plot showed a downward drift after 25% completion. Linearity of the Arrhenius plot held also for all cases. In the case of **4**, the rate constant was calculated using a theoretical infinity titer.

Solvolysis Products. On the basis of GLC and NMR spectroscopy, the solvolysis products of **1**, **2**, and **3** in the carboxamides were identified to be mixtures of adamantanol and adamantyl esters which were furnished by the hydrolysis of initial ion-pair intermediate and of cationic imidate,[1] respectively.

References

1) Part II. S. Saito, T. Yabuki, T. Moriwake, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **51**, 529 (1978).

2) G. R. Reader and J. F. Gormlye, *J. Am. Chem. Soc.*, **73**, 5731 (1951).

3) a) N. Kornblum and R. K. Blackwood, *J. Am. Chem. Soc.*, **78**, 4037 (1956); b) S. D. Ross and M. M. Labes, *ibid.*, **79**, 4155 (1957); c) S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, **83**, 618 (1961); d) J. W. Wilt, R. G. Stein, and W. J. Wagner, *J. Org. Chem.*, **32**, 2097 (1967); e) S. Saito, T. Yabuki, T. Moriwake, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **46**, 1795 (1973); f) M. Anteunis and H. L. Peeters, *J. Org. Chem.*, **40**, 307 (1975); g) H. L. Peeters and M. Anteunis, *ibid.*, **40**, 312 (1975).

4) a) D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 5977 (1970); b) K. Okamoto, M. Matsubara, and T. Kinoshita, *Bull. Chem. Soc. Jpn.*, **45**, 1191 (1972); c) J. M. Harris, D. J. Raber, W. G. Neal, Jr., and M. D. Dukes, *Tetrahedron Lett.*, **1974**, 2331; d) J. M. Harris, D. L. Mount, M. R. Smith, and S. P. McManus, *J. Am. Chem. Soc.*, **99**, 1283 (1977).

5) D. N. Kevill, K. C. Kolwyck, and F. L. Weitl, *J. Am. Chem. Soc.*, **92**, 7300 (1970).

6) a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2538 (1970); b) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970), c) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970); d) T. W. Bentley and P. v. R. Schleyer, *ibid.*, **98**, 7658 (1976); e) F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *ibid.*, **98**, 7667 (1976).

7) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

8) It has been found that *exo*-2-norbornyl-3-*endo*-*d* tosylate rearranges to 7-*anti*-*d* tosylate in a significant extent in the course of solvolysis in DMA (S. Saito, T. Moriwake, K. Takeuchi, and K. Okamoto, submitted for publication in *Bull. Chem. Soc. Jpn.*)

9) St. Landa, S. Kriebel, and E. Knobloch, *Chem. Listy*, **48**, 61 (1954).

10) M. L. Sinnott, H. L. Storesund, and M. C. Whiting, *Chem. Commun.*, **1969**, 1000.

11) a) H. Stetter and C. Wulff, *Chem. Ber.*, **93**, 1366 (1960). b) P. v. R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 182 (1961).

12) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1954).