An average of 39 solvolysis infinities gave a purity of 99.3 ± 0.3% for the sample employed.

Solvents.—Preparation of solvents was described in detail in an earlier paper in this series[5c]; in general, the solvents employed for the rate runs herein reported were from the same batches as those employed[5c] to determine **Y**.

Kinetic Measurements.—The techniques employed for the kinetic runs and halide analysis have been described previously.[5c] Some hydrolysis was found to occur in the case of the benzhydryl halides during the extraction procedure (*e.g.*, 2% hydrolysis in forty shakes of a 5-ml. aliquot of 0.032 *M* benzhydryl chloride in AcOH in 25 ml. of pentane with 10 ml. of H_2O; *ca.* 3% hydrolysis for the bromide under the same conditions). However, it was shown, for benzhydryl chloride, that if rigorous standardization[64] of the extraction procedure[5c] is adhered to, the amount of hydrolysis during extraction is proportional to the concentration of unreacted organic halide present. Under this circumstance, it can be shown that, as long as, in the calculation of the integrated rate constant, all points, and particularly the zero point, are based on the concentration of halide ion obtained *via* the extraction procedure, this hydrolysis has no effect on the magnitude of the rate constants. Thus, if f is the fraction of unreacted RX hydrolyzed during the extraction

$$(a - fa)/[(a - x) - f(a - x)] = a(1 - f)/[(a - x)(1 - f)] = a/(a - x)$$

and, therefore, the integrated rate constant $k = (2.303/t) \log [a/(a - x)]$ is unaffected by such hydrolysis.

TABLE VII

DRIFTS IN RATE CONSTANTS DURING SOLVOLYSIS OF BENZHYDRYL CHLORIDE AT 25°

Solvent	Change in k per 0.01 M reacn., %
90% Dioxane–H_2O	+3
100% AcOH[a]	0
95% AcOH-HCOOH[b]	−5
90% AcOH-HCOOH[b]	−8
85% AcOH-HCOOH[b]	−11
75% AcOH-HCOOH[a]	−16
4 M H_2O in AcOH[a]	−5

[a] Contained 0.068 *M* lithium acetate and/or formate. [b] Contained 0.038 *M* lithium acetate and/or formate.

Experimental Results.—The new data reported in Table I were based on an average of 7 points per run followed past 50 to 80% of completion. The average deviation for all of the rates which were first order within experimental error was ±0.9% for benzhydryl chloride and ±1.0% for the bromide. For the rate runs which drifted, the entries in Table I, suitably footnoted, are the estimated initial rates. These estimates were made empirically by linear extrapolation to zero reaction of a plot of integrated rate constant *versus* percentage reaction. The magnitudes of these drifts, expressed empirically as percentage change in k per 0.01 *M* reaction calculated from the true zero of reaction time, are listed in Table VII. The drifts are manifestations of opposing salt effects, and they will be considered more fully in a later paper.

LOS ANGELES 24, CALIF.

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[64] The extent of hydrolysis was shown to depend on the number of shakes employed in the first aqueous extraction.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

The Solvolyses of Some Tertiary Halides in Dimethylformamide and N-Methylpropionamide

BY SIDNEY D. ROSS AND MORTIMER M. LABES

RECEIVED FEBRUARY 27, 1957

The solvolyses of *t*-butyl bromide and dimethylneopentylcarbinyl chloride have been studied in both N-methylpropionamide and dimethylformamide, and *t*-butyl chloride has been studied in the latter solvent. The results obtained are discussed in terms of current mechanisms for solvolytic reactions.

There has been considerable interest recently in dimethylformamide as a medium for organic reactions.[1] The attractive properties of dimethylformamide are its exceptional solvent power for both organic and inorganic compounds and its high polarity, as indicated by its dielectric constant of 36.71 at 25°.[2] In this latter respect, N-methylpropionamide, which has received very little attention, perhaps because it is not available commercially, is of even greater interest, since its dielectric constant at 30° is 164.3,[2] a value more than twice that of the dielectric constant of water.

Because of these highly polar characteristics, dimethylformamide and N-methylpropionamide might be expected to be particularly effective solvents for S_N1 solvolyses.[3] To explore this possibility, we have studied the rates of solvolysis of three tertiary, aliphatic halides, *t*-butyl chloride, *t*-butyl bromide and dimethylneopentylcarbinyl chloride, in these two solvents. Since the inception of this work, some results on the reaction of *t*-butyl bromide in dimethylformamide have appeared in the literature.[1d]

Experimental

Materials.—Eastman Kodak Co. White Label *t*-butyl bromide and *t*-butyl chloride were distilled from phosphorus pentoxide prior to use, b.p.'s 72–73° and 50–51°, respectively. Dimethylneopentylcarbinyl chloride was prepared by the procedure described in the literature[4]; b.p. 51.5–53° at 28 mm., $n^{20}D$ 1.4308. Eimer and Amend, C.P. sodium bromide was dried in a vacuum oven over phosphorus pentoxide for two days prior to use. Eastman Kodak Co. White Label tetraethylammonium bromide was crystallized from isopropyl alcohol and dried *in vacuo*. Tetraethylammonium nitrate was prepared by adding equivalent nitric acid to a 10% aqueous solution of tetraethylammonium hydroxide (Eastman Kodak Co.). The solution was concentrated by distillation at a water-pump vacuum, and the salt which crystallized was recrystallized two times from isopropyl alcohol and dried *in vacuo;* m.p. 280° dec.[5]

N,N-Dimethylformamide (du Pont technical grade) was

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[1] (a) E. Rochow and K. Gingold, THIS JOURNAL, **76**, 4852 (1954). (b) N. Kornblum, H. O. Larsen, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto and G. E. Graham, *ibid.*, **78**, 1497 (1956). (c) H. K. Hall, Jr., *ibid.*, **78**, 2717 (1956). (d) N. Kornblum and R. K. Blackwood, *ibid.*, **78**, 4037 (1956).

[2] G. R. Leader and J. F. Gormley, *ibid.*, **73**, 5731 (1951).

[3] E. D. Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

[4] (a) F. C. Whitmore and H. A. Southgate, THIS JOURNAL, **60**, 2572 (1938); F. C. Whitmore, C. D. Wilson, J. V. Capinjola, C. O. Tongberg, G. H. Fleming, R. V. McGrew and J. N. Cosby, *ibid.*, **63**, 2035 (1941). (b) H. C. Brown and H. L. Berneis, *ibid.*, **75**, 10 (1953).

[5] L. M. Tucker and C. A. Kraus, *ibid.*, **69**, 454 (1947).

distilled from calcium oxide; b.p. 45–46° at 12–13 mm., $n^{25}D$ 1.4299, specific resistance 1.7 × 10^6 ohm-cm. N-Methylpropionamide was prepared according to D'Alelio and Reid[6] and distilled from calcium oxide before use; b.p. 103° at 12-13 mm., $n^{25}D$ 1.4340, specific resistance 8.3 × 10^5 ohm-cm. The latter solvent contained 0.002–0.008% water by volume, the former 0.09–0.13% water, as determined by Karl Fischer titration in both cases.

Rate Measurements.—All of the reacting solutions were kept in thermostats which maintained the temperatures given in Tables I and II to ±0.1°. The reactions were run either in glass-stoppered flasks from which aliquots were taken at appropriate time intervals or individual aliquots were sealed in glass ampoules, which were then placed in the thermostats. Aliquots were quenched by adding them to benzene, and the benzene solution was extracted first with dilute nitric acid and then two times with distilled water. Except as otherwise indicated in Tables I and II, the aqueous extracts were analyzed for halide ion by the Volhard method for runs in which the initial concentrations of organic halide were greater than 0.02 *M*, and by potentiometric titration using a silver–silver halide electrode and a Leeds–Northrup type K-2 potentiometer where the initial concentrations of organic halide were below 0.02 *M*.

In the one run where the olefin formed was determined as a function of time, the ampoules, containing a 5-ml. aliquot, were broken under 100 ml. of carbon tetrachloride containing 10 ml. of a freshly standardized solution of bromine in carbon tetrachloride. This solution was allowed to stand 30 minutes, 10 ml. of 10% aqueous potassium iodide was added and the liberated iodine was titrated with standard thiosulfate solution. This same procedure was used in determining infinity olefin titers.

TABLE I

REACTION RATES IN DIMETHYLFORMAMIDE

Compound	Initial concn., mole l.$^{-1}$	*T*, °C.	Added salt, mole l.$^{-1}$	$k \times 10^5$, sec.$^{-1}$	Final % olefin[c]
t-BuCl	0.0875	50.7		0.0095 ± 0.0011	
t-BuCl	.0648	80.0		.244 ± 0.003	
DNCCl[d]	.0137	24.8		.012 ± 0.001	
DNCCl	.0725	24.8		.014 ± 0.002	
DNCCl	.0760[b]	24.8		.014 ± 0.002	
t-BuBr	.0835[b]	24.8		.26 ± 0.01	
t-BuBr	.1710[b]	40.3		1.6 ± 0.1	
t-BuBr	.1580[a]	40.3		1.40 ± 0.1	84
t-BuBr	.00917	50.7		4.27 ± 0.02	
t-BuBr	.0855	50.7		5.2 ± 0.2	94
t-BuBr	.0835	50.7	0.0083 Et_4N^+, NO_3^-	5.2 ± 0.2	85
t-BuBr	.0837	50.7	.0417 Et_4N^+, NO_3^-	5.7 ± 0.2	90
t-BuBr	.0828	50.7	.0970 Et_4N^+, NO_3^-	7.0 ± 0.2	101
t-BuBr	.0852	50.7	.1668 Et_4N^+, NO_3^-	8.0 ± 0.2	89
t-BuBr	.0830	50.7	.1035 NaBr	8.7 ± 0.2	85
t-BuBr	.0858	50.7	.0760 Et_4N^+, Br^-	7.7 ± 0.1	

[a] The rate was measured by determining olefin as a function of time. [b] Run conducted in glass-stoppered flask. All other runs were in sealed tubes. [c] Measured after at least ten half-lives. [d] Abbreviation for dimethylneopentylcarbinyl chloride.

TABLE II

REACTION RATES IN N-METHYLPROPIONAMIDE

Compound	Initial concn., mole l.$^{-1}$	*T*, °C.	Added salt, mole l.$^{-1}$	$k \times 10^5$, sec.$^{-1}$
DNCCl[c]	0.0126	24.8		0.044 ± 0.002
DNCCl	.0880[b]	24.8		.045 ± 0.002
t-BuBr	.0137[b]	24.8		.23 ± 0.03
t-BuBr	.0955[a]	39.2		.12 ± 0.01
t-BuBr	.197	39.2		.13 ± 0.01
t-BuBr	.0785	50.7		5.0 ± 0.2
t-BuBr	.0810	50.7	0.1002 Et_4N^+, NO_3^-	5.4 ± 0.1
t-BuBr	.0788	50.7	0.0922 Et_4N^+, Br^-	4.9 ± 0.2

[a] Final olefin titer = 97%. [b] Run conducted in glass-stoppered flask. All other runs were in sealed tubes. [c] Abbreviation for dimethylneopentylcarbinyl chloride.

Results

The results of all the rate studies in dimethylformamide are compiled in Table I, and the rates in N-methylpropionamide are given in Table II. In the case of *t*-butyl bromide, the product results almost entirely from an elimination reaction, as indicated by the final olefin titers and the fact that, in the one case where the rate was followed by titrating for the olefin formed, the rate constant does not differ appreciably from the rate constant obtained by halide titration.[7] It is also probable that small amounts of *t*-butyl alcohol are formed in these reactions as a result of the traces of moisture present in the two solvents.

Some typical data for the reaction of *t*-butyl bromide in dimethylformamide are given in Tables III and IV and in Table V for the same halide in N-methylpropionamide. At low halide concentrations in dimethylformamide (Table III) and at all halide concentrations in N-methylpropionamide, the instantaneous rate constants show no trend with time. At higher initial halide concentrations in dimethylformamide (Table IV), the instantaneous rate constants increase with time. This is due to the operation of a positive salt effect as shown in Fig. 1. The ionic strengths shown in this plot are the concentrations of the added salts plus one-half the initial *t*-butyl bromide concentrations, *i.e.*, the ionic strength at 50% reaction.

It is particularly noteworthy that the two bromides accelerate the rate more strongly than does tetraethylammonium nitrate. Spieth and Olson[8] have reported similar results for *t*-butyl bromide in aqueous acetone with added lithium perchlorate, lithium bromide and lithium chloride. All three salts accelerated the rate, with the perchlorate having the largest effect and the chloride the least effect. In connection with our data, we consider it

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[6] G. F. D'Alelio and E. E. Reid, THIS JOURNAL, **59**, 109 (1937).

[7] This result does not necessarily contradict Kornblum and Blackwood's[1d] isolation of only a 46% yield of isobutylene from the reaction of *t*-butyl bromide in dimethylformamide, since the losses on isolation may be substantial.

[8] F. Spieth and A. R. Olson, THIS JOURNAL, **77**, 1412 (1955).

TABLE III

SOLVOLYSIS OF 0.00917 *M* *t*-BUTYL BROMIDE IN DIMETHYLFORMAMIDE AT 50.7 ± 0.1°

Time, hr.	Reaction, %	$k \times 10^5$, sec.$^{-1}$
1.0	14.2	4.25
2.0	26.0	4.28
3.0	36.9	4.26
4.1	46.5	4.27
5.0	54.0	4.31
7.0	66.0	4.28

TABLE IV

SOLVOLYSIS OF 0.0855 *M* *t*-BUTYL BROMIDE IN DIMETHYLFORMAMIDE AT 50.7 ± 0.1°

Time, hr.	Reaction, %	$k \times 10^5$, sec.$^{-1}$
1.0	15.8	4.78
2.0	29.8	4.91
3.5	47.4	5.10
5.0	60.8	5.20
7.5	77.8	5.57

TABLE V

SOLVOLYSIS OF 0.0785 *M* *t*-BUTYL BROMIDE IN N-METHYLPROPIONAMIDE AT 50.7 ± 0.1°

Time, hr.	Reaction, %	$k \times 10^5$, sec.$^{-1}$
1.00	17.2	5.25
1.75	26.7	4.93
2.75	38.9	4.93
4.00	50.3	4.85
5.50	63.2	5.05
7.00	72.0	5.05

pertinent that conductivity measurements on potassium nitrate and potassium bromide in dimethylformamide at 25°[9] indicate that the bromide is much less associated than is the nitrate in this solvent, since the bromide shows only a small deviation from the calculated, limiting Onsager slope, whereas the nitrate shows a very sizable deviation. This suggests that the differences that we observe between bromides and nitrates may be due, in part at least, to differences in the extent of ion-pairing. At any rate, there is no evidence for any retardation of the rate by bromide ion. In dimethylformamide there is a clear acceleration of the rate with added bromide ion. In N-methylpropionamide, the instantaneous rate constants are constant with time, and a run with added tetraethylammonium bromide shows no significant slowing of the rate.

Discussion

The usual description of the mechanism of solvolysis reactions is in terms of the S_N1–S_N2 (and/or E_1–E_2) classification of the Hughes–Ingold school.[3,10] The S_N1 and E_1 reactions involve a rate-determining ionization to a cationic intermediate. The solvent functions, largely in an electrophilic manner, to heterolyze the C–X bond and solvate the anion, and no covalent interaction between the cation and the solvent is required. The S_N2 and E_2 mechanisms, on the other hand, involve a concerted process, in which the solvent functions both by virtue of its ionizing power and its nucleophilic character.

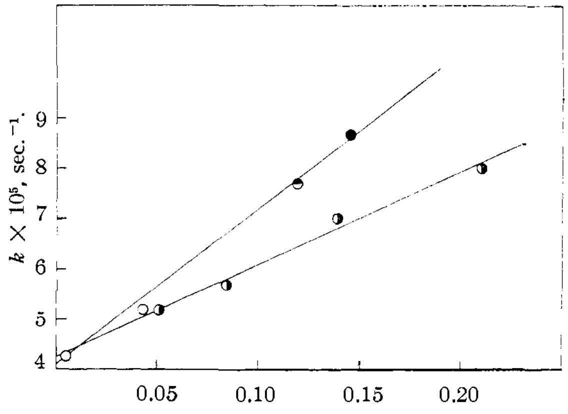

Fig. 1.—Salt effect in the solvolysis of *t*-butyl bromide in dimethylformamide at 50.7 ± 0.1°: ○, nothing added; ◑, tetraethylammonium nitrate added; ◓, tetraethylammonium bromide added; ●, sodium bromide added.

It is now generally recognized that these reaction categories are limiting mechanistic extremes of a gradation of mechanisms, reflecting a continuous spectrum of transition states. The existence of borderline or intermediate cases has been recognized by the Hughes–Ingold school.[10,11] Winstein, Grunwald, *et al.*, classify all cases in which there is evidence both for an intermediate and covalent interaction of the cation with the solvent as borderline cases and have discussed these in terms of the canonical structures, I, II and III, contributing to the transition state.[12] Swain and his coworkers[13] have emphasized the importance of ion–dipole solvation bonds to the cation as well as co-

$$\underset{\text{I}}{\text{Z: R–X}} \qquad \underset{\text{II}}{\text{Z–R: X}} \qquad \underset{\text{III}}{\text{Z: R}^+\text{: X}}$$

valent solvation bonds to the cation and have argued that, in almost all solvolytic reactions, the solvent is involved in both a nucleophilic and an electrophilic capacity.

A striking feature of the solvolysis reactions in dimethylformamide and N-methylpropionamide is that they are unexpectedly slow, even if one allows that these solvents do not rival hydroxylic solvents in their capacity for electrostatic solvation.[14] More striking, the rates in the two solvents are very similar in spite of the fivefold difference in dielectric constant. Nevertheless, the activation energies in these solvents are the ones usually obtained for these halides.[12] We have rate data at three temperatures in both solvents for *t*-butyl bromide and at two temperatures in dimethylformamide for *t*-

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[9] D. P. Ames and P. G. Sears, *J. Phys. Chem.*, **59**, 16 (1955).

[10] E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

[11] E. D. Hughes, C. K. Ingold and U. G. Shapiro, *J. Chem. Soc.*, 225 (1936); M. L. Dhar, E. D. Hughes and C. K. Ingold, *ibid.*, 2058 (1948).

[12] E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948); S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951); A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

[13] (a) C. G. Swain, *ibid.*, **70**, 1119, 2989 (1938). (b) C. G. Swain and R. B. Mosely, *ibid.*, **77**, 3727 (1955); C. G. Swain, R. B. Mosely and D. E. Bown, *ibid.*, **77**, 3731 (1955); C. G. Swain, D. C. Dittmer and L. E. Kaiser, *ibid.*, **77**, 3737 (1955).

[14] E. Gelles, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2918 (1954).

butyl chloride. For *t*-butyl bromide, these result in activation energies of 23 ± 1 kcal. in N-methylpropionamide and 22.1 ± 0.5 kcal. in dimethylformamide. For *t*-butyl chloride in dimethylformamide the activation energy is 25 ± 1 kcal.

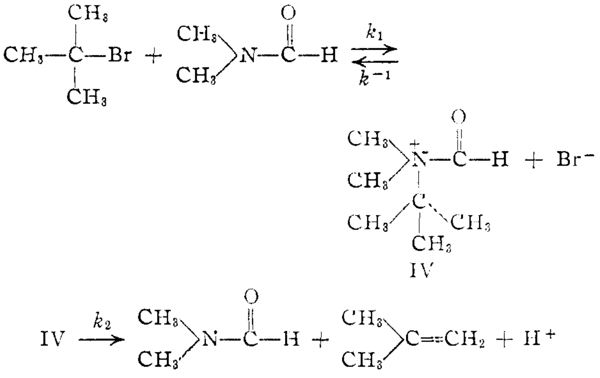
As another criterion of mechanism, we have applied the Winstein–Grunwald equation[12] to our data. According to this equation

$$\log k = \log k_0 + mY$$

the difference in the logarithms of the rate constants for the first order solvolysis of a given substance in a solvent and in the standard solvent, 80% aqueous ethanol, is the product of two parameters, *m*, the compound parameter, and *Y*, a measure of the ionizing power of the solvent. Since the *m*'s and log k_0's are known[4b,12] for all three halides, we can calculate *Y*-values for both solvents. For dimethylformamide, we can obtain three *Y*-values, one for each halide on which we have rate data. The resulting values for *Y* are −3.47 from *t*-butyl chloride, −2.46 from *t*-butyl bromide and −3.72 from dimethylneopentylcarbinyl chloride. Similarly, for N-methylpropionamide, we can obtain two *Y*-values, −2.60 from our rate data with *t*-butyl bromide and −3.14 from our rate data with dimethylneopentylcarbinyl chloride. Clearly, our rate results are not correlated satisfactorily by the Winstein–Grunwald equation. However, in spite of the impressive success achieved by the Winstein–Grunwald equation in correlating the rates of solvolysis of organic halides with solvent change and the usefulness of this equation in diagnosing solvolytic mechanisms, it does not follow that an absence of correlation, in a particular instance, necessitates a basic difference in mechanism.

This point has been emphasized in a searching and cogent analysis of the Winstein–Grunwald relation by Wilputte-Steinert and Fierens.[15] As these authors have indicated, for a given halide *m* cannot be expected to be constant in all solvents, since the delocalization of charge must produce variable perturbations which depend on the nature and composition of the solvent.[16] Also, the ionizing power, *Y*, is not an intrinsic property of the solvent. The solvation process is not limited to the carbon–chlorine bond. It must involve the entire circumference of the halide structure and, as the halide structures are varied, there must result differences in the degree of solvation of the initial states and transition states.

The reactions of halides in dimethylformamide have been discussed in terms of an intermediate or product involving covalent bonding of the cation to the solvent.[1c,d] For the solvolysis of *t*-butyl bromide in dimethylformamide, one might write[17]

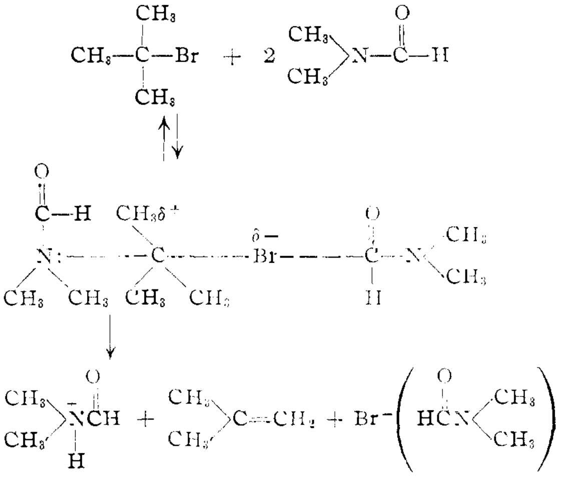


As written, this mechanism suggests a backside attack by the solvent on the C–Br bond. However, it is possible that IV results from a frontside attack as the C–Br bond is being broken. If we assume a steady state with respect to IV, the rate expression is

$$\text{rate} = \frac{k_1k_2(\text{bromide})}{k_{-1}(\text{Br}^-)} + k_2$$

Since, in this case, there is no slowing of the rate by added bromide ion and since the rate of bromide ion liberation is equal to the rate of olefin formation, $k_2 >> k^{-1}(\text{Br}^-)$, and the rate ≅ k_1(bromide).[18]

In addition, there is the possibility of a concerted elimination reaction involving two or more solvent molecules. This type of mechanism was first suggested by Holysz,[19] who studied the dehydrohalogenation of 4-halo-3-ketosteroids in dimethylformamide. This mechanism might be represented as



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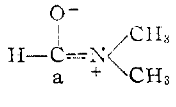
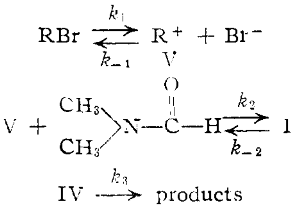
[15] L. Wilputte-Steinert and P. J. C. Fierens, *Bull. soc. chim. Belg.*, **64**, 308 (1955).

[16] In this connection, it is pertinent to point out that the substituent constants in the Hammett equation vary markedly with solvent changes; H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[17] In structure IV we have followed the previous practice[1c,d] of making the nitrogen atom the nucleophilic center of the dimethylformamide molecule. As was pointed out by a referee, it is also probable that, in dimethylformamide, the nitrogen acts electrophilically and the oxygen nucleophilically. Dimethylformamide shows restricted rotation about its carbon–nitrogen bond (W. D. Phillips, *J. Chem. Phys.*, **23**, 1363 (1955); H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1956)) suggesting a large contribution from structure a.



[18] A variation of this mechanism is



$$\text{RBr} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\text{V}}{\text{R}^+} + \text{Br}^-$$

$$\text{V} + (\text{CH}_3)_2\text{N—C(=O)—H} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \text{IV}$$

$$\text{IV} \xrightarrow{k_3} \text{products}$$

If we assume a steady state with respect to both IV and V and, further, that terms involving ($k_{-1}(\text{Br}^-)$) are negligible with respect to the other terms present, we again find that rate ≅ k_1(bromide).

[19] R. P. Holysz, This Journal, **75**, 4432 (1953).

Although this mechanism has been depicted as involving only two solvent molecules, it is possible that more than two are involved or, alternatively, that a single solvent molecule is involved in a cyclic transition state as suggested by Kornblum and Blackwood.[1d] In this case, too, the roles of the oxygen and nitrogen atoms of dimethylformamide may be reversed.[17] Also, the ion–dipole solvation bond to carbon may be from the front rather than the rear. In any case, the kinetics would be those observed.

Our results do not permit us to make a choice between these possibilities. It is clear that there may be solvolytic reactions in which the solvent functions in a purely electrophilic manner. It is equally probable that there are solvolytic mechanisms in which the action of the solvent is entirely nucleophilic. Between these two extremes there must be a broad range of mechanisms in which two or more solvent molecules are involved and in which the solvent acts both electrophilically and nucleophilically. These mechanisms, thus, reflect an equally broad and continuous spectrum of transition states differing in the configurations of the solvating solvent molecules and are best considered as differing in degree but not in kind.

NORTH ADAMS, MASS.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Perfluoroalkylzinc Compounds. I. The Preparation and Properties of Perfluoroalkylzinc Halides[1,2]

BY WILLIAM T. MILLER, JR., ELLIOT BERGMAN[3] AND ARNOLD H. FAINBERG

RECEIVED JANUARY 30, 1957

Convenient methods for the preparation of perfluoroalkylzinc compounds of the type R_FCF_2ZnI (solvated) are described together with the results of related work on the reactions of fluoroperhaloalkyl bromides and iodides with metallic zinc. The perfluoroalkylzinc iodides as exemplified by perfluoro-*n*-propylzinc iodide are shown to be thermally stable in solution and inert to carbon dioxide and to oxygen. They are strong Lewis acids, in contrast to the alkylzinc iodides. They are readily hydrolyzed, cleaved by halogen and converted into olefins by pyrolysis. They are unreactive with organic electrophiles, but under vigorous conditions in the presence of such compounds containing active hydrogen they tend to yield R_FCF_2H rather than addition products.

Introduction

Evidence for the existence of perhaloalkylzinc compounds was first obtained in attempting to dehalogenate fluoroperhalo compounds which do not contain halogens other than fluorine in the 1,2-relation to produce olefins. Reduced products were isolated by hydrolysis of reaction mixtures under conditions which suggested the intermediate formation of perhalo zinc compounds.[4] Efforts were then made to prepare perfluoroalkylzinc compounds, and it was found that perfluoro-*n*-propylzinc iodide could be obtained readily in dioxane solution.[5] The present paper presents work on the preparation and properties of solvated perfluoroalkylzinc compounds of the type R_FCF_2-ZnX and on related reactions of fluoroperhaloalkyl iodides and bromides with metallic zinc.

The preparation of solutions of zinc and cadmium perfluoroalkyls from trifluoromethyl iodide and heptafluoro-*n*-propyl iodide has been reported independently by Haszeldine[6] with experimental work on heptafluoro-*n*-propylzinc iodide appearing more recently.[7] Earlier attempts by Emeléus and Haszeldine to prepare organozinc compounds from trifluoroiodomethane and pentafluoroiodoethane yielded only fluoroform and pentafluoroethane as organic products.[8]

Discussion and Results

In the present work all of the fluoroperhaloalkyl iodides and bromides tested were found to react with zinc dust in donor-type solvents such as aliphatic ethers and pyridine at or below reflux temperatures. Depending upon the structure of the perhaloalkyl halide and the choice of solvent and reaction conditions, one or more products of the type shown below were isolated. Organozinc compounds have been obtained only when Y is fluorine. When Y is chlorine intramolecular dehalogenation ordinarily occurs readily and always with great ease when Y is bromine or iodine.

$$\begin{array}{lrl} R_FCFYCF_2X + Zn & \xrightarrow{\text{solvent}} R_FCF{=}CF_2 & \text{(I)} \\ X = \text{Br or I} & R_FCFYCF_2ZnX & \text{(II)} \\ Y = \text{F or other halogen} & R_FCFYCHF_2 & \text{(III)} \\ & [R_FCFYCF_2\text{-}]_2 & \text{(IV)} \end{array}$$

Perfluoro-*n*-propyl iodide was found to react readily with zinc in dioxane to yield more than 75% perfluoro-*n*-propylzinc iodide (II) plus small amounts of heptafluoropropane (III). Perfluoro-*n*-propyl bromide reacted in 1,2-dimethoxyethane after a long induction period to yield 60% of the corresponding zinc compound (II). Perfluoro-*n*-pentyl iodide reacted sluggishly with zinc in dioxane to yield a mixture of perfluoro-*n*-pentylzinc iodide (II), undecafluoro-*n*-pentane (III) and perfluoro-*n*-decane (IV). The perhalomethanes failed to

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[1] Taken, in part, from a thesis submitted by Elliot Bergman to the Graduate School, Cornell University, Ithaca, N. Y., June, 1955.

[2] This research was supported in part by the Office of Naval Research.

[3] Procter and Gamble Fellow, 1953–1954.

[4] A. H. Fainberg and W. T. Miller, Jr., Abstracts of Papers, 120th Meeting, American Chemical Society, New York, N. Y., Sept., 1951, p. 7K; W. T. Miller, Jr., and J. M. Howald, unpublished work.

[5] W. T. Miller, Jr., A. H. Fainberg and E. Bergman, Abstracts of Papers, 122nd Meeting, American Chemical Society, Atlantic City, N. J., Sept., 1952, p. 14-K.

[6] R. N. Haszeldine, *Nature*, **168**, 1028 (1951).

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