Solvolysis of 1-Chloro-1-nitro-1-phenylethane and Its Derivatives[1]

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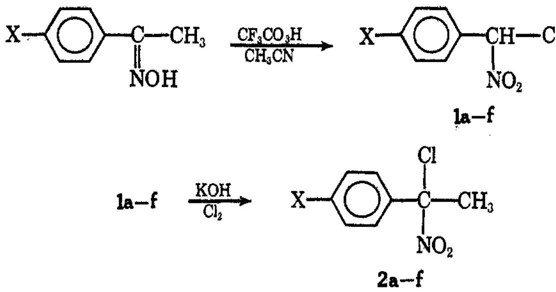
The solvolyses of five 1-chloro-1-nitro-1-(*p*-X-phenyl)ethanes (X = CH_3, H, Cl, Br, NO_2), **2a–e**, respectively, have been studied in 50 and 80% aqueous ethanol and in 90% formic acid. A linear Hammett correlation utilizing σ^+ values was obtained in 50% ($\rho = -1.52$; $r = -0.9976$) and 80% ($\rho = -1.62$; $r = -0.9959$) aqueous ethanol for **2b–e**. The methyl derivative **2a** hydrolyzed faster in these solvents than predicted from its σ^+ value and the ρ values mentioned. In 90% formic acid, however, the rates of solvolysis of **2a**, **2b**, **2d**, and **2e** were all correlated well with σ^+ values ($\rho = -3.73$; $r = -0.9951$). It is suggested that, as is the case in the solvolysis of other benzylic systems, two mechanisms are involved in the more nucleophilic aqueous ethanol solvents, with those compounds containing electron-withdrawing substituents requiring nucleophilic involvement of solvent molecules. In the less nucleophilic but highly ionizing formic acid solvent, a single mechanism involving a high degree of carbonium ion character prevails for all compounds. Anchimeric assistance by the nitro group is apparently not involved in these solvolyses.

A nitro group conjugated with a reaction center strongly inhibits carbonium ion formation in S_N1 solvolyses. In alcoholysis, *p*-nitrobenzyl halides react at a rate one-tenth to one-twentieth that of the corresponding benzyl halides.[2,3] Similarly, *p*-nitrobenzhydryl chloride undergoes alcoholysis much more slowly than benzhydryl chloride, the relative rate being 0.00069.[4,5] These findings lead to the expectation that α-halonitro compounds, in which the nitro group is attached directly to the reaction site, should solvolyze very sluggishly. This expectation is substantiated by the work of Simonetta, Favini, and Carra with 2-chloro-2-nitropropane, which ionizes very slowly even at 90° in the presence of an excess of silver ion.[6] In contrast, however, Norten and Slater found that α-nitrobenzhydryl chloride (**3**) ionizes in 80% ethanol at about the same rate that *p*-nitrobenzhydryl chloride would be expected to ionize.[7] This unanticipated finding prompted the present exploration of the possibility of anchimeric assistance to ionization by the nitro group. Nitro group participation has been utilized to explain unexpectedly large differences in reactivity between *o*-nitro and *p*-nitro benzyl and benzhydryl systems. Kim, Friedrich, Andrews, and Keefer report that for the acetolysis at 25° of *o*-nitrobenzhydryl bromide and *p*-nitrobenzhydryl bromide the rate constant ratio, $k_{\text{ortho}}/k_{\text{para}}$, is approximately 3000.[8] Similarly, for the dissociation rates of the isomeric nitroiodobenzene dichlorides, the rate constant ratio in acetic acid at 25° is of the order of 1000.[9] From this work it is apparent that nitro group participation can be expected in those systems in which the geometry is favorable, although the solvolysis in ethanol–water mixtures of *o*-nitrobenzyl chloride represents an apparent anomaly in this respect.[10]

The work of Kemp and Metzger[11] and of Bordwell and Knipe[12,13] suggested a possible approach to the problem. The ρ value for hydrolysis of substituted α-bromophenylacetates was shown to be relatively insensitive to salt and medium effects, and this was interpreted as resulting from intramolecular electrostatic interaction of the carboxylate ion with the incipient carbonium ion center. Accordingly, a study of solvent effects on the magnitude of ρ for the hydrolysis of a series of 1-chloro-1-nitro-1-(*p*-X-phenyl)ethanes might provide information bearing on the possibility of nitro group participation.

Results and Discussion

Six 1-chloro-1-nitro-1-(*p*-X-phenyl)ethanes, **2a–f**, were prepared as shown in the following equations. Oxidation of the appropriate oximes of para-substituted acetophenones gave 1-nitro-1-(*p*-X-phenyl)ethanes, **1a–f**, which were converted to the nitronate anions in basic solution and allowed to react with chlorine to produce **2a–f**.[14] Of the halonitro compounds, the *p*-methoxy derivative, **2f**, proved to be unstable and decomposed on standing at room temperature with the evolution of a brown gas. Although the spectral data for this compound (see Experimental Section) substantiated its structure, the rapid decomposition precluded elemental analysis and solvolysis studies. Compounds **2a–d** are oils which were purified by elution chromatog-



1a–f

2a–f

a, X = CH_3 **d**, X = Br
b, X = H **e**, X = NO_2
c, X = Cl **f**, X = CH_3O

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[1] Abstracted in part from the Ph.D. dissertation of L. W. Harrison, Memphis State University, Dec 1970.

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[7] D. G. Norten and C. D. Slater, *Tetrahedron Lett.*, 3699 (1968).

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[10] J. B. Hyne and R. Wills, *J. Amer. Chem. Soc.*, **85**, 3650 (1963).

[11] K. C. Kemp and D. Metzger, *J. Org. Chem.*, **33**, 4165 (1968).

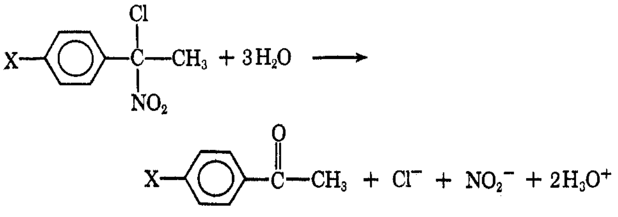
[12] F. G. Bordwell and A. C. Knipe, *ibid.*, **35**, 2956 (1970).

[13] F. G. Bordwell and A. C. Knipe, *ibid.*, **35**, 2959 (1970).

[14] The syntheses of the nitro compounds utilized in this study have recently been reported by F. G. Bordwell, W. J. Boyle, Jr., and K. C. Yee [*J. Amer. Chem. Soc.*, **92**, 5926 (1970)]. They have also been synthesized by an alternative route: M. Fukuyama, P. W. K. Flanagan, F. T. Williams, L. Frainier, S. A. Miller, and H. Shechter, *ibid.*, **92**, 4689 (1970).

raphy using Florisil, and **2e** is a solid that was purified by recrystallization from aqueous ethanol

The stoichiometry of the hydrolysis of **2a–e** is given in the equation. In aqueous ethanol solutions the hydrolyses were followed by an ultraviolet spectrophotometric



technique based on the absorbance changes resulting from the production of the substituted acetophenones. The reactions were usually followed to approximately 60% completion, and good, first-order kinetics were observed in all cases. The calculated infinity readings generally agreed quite closely with those observed after several half-lives, which indicated that the ketones were produced quantitatively. Spectrophotometric analysis of the reaction of **2e** was precluded by its strong absorption at 257 nm (ϵ 11,500) which masked the developing absorption of *p*-nitroacetophenone at 263 nm (ϵ 12,600). This hydrolysis was therefore followed by a titrimetric method for chloride ion. All runs in 90% formic acid were analyzed by the titrimetric method because of the intensity of the end absorption of the formic acid contained in the diluted samples. Spectrophotometric examination of a reaction mixture of **2a** after 16 half-lives revealed that in 90% formic acid *p*-methylacetophenone was produced quantitatively, but the analysis involved measurements on the steep part of the end-absorption curve, such that the spectrophotometric method appeared to be less desirable than the titrimetric method for kinetic measurements. The equivalency of the methods was demonstrated by titrimetric runs using compound **2a** in 50% ethanol at 50.0°. The rate constants obtained by both methods (see Table I) agreed within 12%.

The rate of hydrolysis of 1-chloro-1-nitro-1-(*p*-nitrophenyl)ethane (**2e**) in 80% ethanol was so slow that it was inconvenient to measure. The rate constant in this solvent was calculated from the rates in 50 and 40% ethanol using the Winstein–Grunwald equation.[15] Several attempts were made to measure the rate of hydrolysis of the unstable 1-chloro-1-nitro-1-(*p*-anisyl)ethane (**2f**). Hydrolysis in 50% ethanol at 30° produced *p*-methoxyacetophenone but did not show good first-order kinetics.

The rate constants determined in the various solvents and at different temperatures are collected in Table I. A comparison of the general magnitude of those rate constants to those of the corresponding benzyl chlorides shows about the same relationship as revealed by comparison of the rate constant for hydrolysis of chlorodiphenylnitromethane (α-nitrobenzhydryl chloride) (**3**) with that of benzhydryl chloride. Specifically, the relative rate of solvolysis in 80% ethanol at 25° for α-nitrobenzhydryl chloride[7] compared to benzhydryl chloride[16] is 4.88×10^{-4}, whereas at 50° the relative rate for 1-chloro-1-nitro-1-phenylethane compared to α-phenylethyl chloride[17] is 2.74×10^{-4}. This suggests that the α-nitro group produces in both the benzhydryl and benzyl systems the same change in degree of carbonium ion character in the transition state leading to solvolysis.

TABLE I

SOLVOLYSIS OF 1-CHLORO-1-NITRO-1-(*p*-X-PHENYL)ETHANES

X	Solvent[a]	Temp, °C	k_1, sec^{-1}	n[b]	% devn[c]
CH_3	50% ethanol	80.0	2.49×10^{-4}	5	2.9
		65.0	5.55×10^{-5}	3	2.9
		50.0[d]	1.03×10^{-5}	3	0.9
		50.0[e]	0.91×10^{-5}	2	2.8
	80% ethanol	80.0	1.76×10^{-4}	2	0.5
	90% formic acid	50.0	4.32×10^{-4}	2	0.0
		40.0	1.46×10^{-4}	2	1.2
H	50% ethanol	80.0	1.19×10^{-5}	5	4.7
		65.0	2.21×10^{-6}	3	1.7
		50.0	2.91×10^{-7}	5	3.7
	80% ethanol	80.0	1.84×10^{-6}	2	1.5
	90% formic acid	80.0	6.12×10^{-4}	2	4.6
Cl	50% ethanol	80.0	8.53×10^{-6}	3	0.8
		65.0	1.36×10^{-6}	3	3.0
		50.0	1.96×10^{-7}	3	3.6
	80% ethanol	80.0	1.46×10^{-6}	2	0.9
Br	50% ethanol	80.0	6.04×10^{-6}	4	7.0
		65.0	1.14×10^{-6}	3	1.4
		50.0	1.52×10^{-7}	3	0.8
	80% ethanol	80.0	9.42×10^{-7}	2	7.5
	90% formic acid	80.0	3.44×10^{-4}	2	1.8
NO_2	40% ethanol	80.0	1.41×10^{-6}	1	
	50% ethanol	80.0	7.35×10^{-7}	3	3.4
	80% ethanol	80.0	8.99×10^{-8}	. . .[f]	
	90% formic acid	80.0	6.35×10^{-7}	2	2.7

[a] Volume per cent. All runs in aqueous ethanol contained 0.05 mol/l. of $NaClO_4$, and those in formic acid contained 0.065 mol/l. of $NaClO_4$. [b] Number of runs. [c] Standard deviation expressed in per cent. [d] Determined spectrophotometrically. [e] Determined titrimetrically. [f] This value was obtained by application of the Winstein–Grunwald equation using the values obtained in 40 and 50% ethanol.

Substitutuent Effects.—The substituents employed represent a reasonable range of electronic character from the strongly electron-withdrawing nitro group ($\sigma^+ = +0.79$) to the electron-donating methyl group ($\sigma^+ = -0.31$).[18] In both 50 and 80% ethanol the *p*-methyl derivative hydrolyzed much faster than would be expected from its σ^+ value and the ρ value obtained for the other substituents. The rates for compounds **2b–e** are well-correlated in both solvents, however, with $\rho = -1.52$ ($r = -0.9976$) in 50% ethanol, and $\rho = -1.62$ ($r = -0.9959$) in 80% ethanol. A σ^+ value of -0.87 in 50% ethanol and of -1.16 in 80% ethanol would be required to place the *p*-methyl derivative on the least square lines. The use of σ or σ^- values provides an even less satisfactory correlation, and, in keeping with the analogous deviation of compounds containing electron-donating substituents in various other solvolyses of benzylic systems (*vide infra*), it is apparent from the overall direction of substituent effects on the rates of the present solvolyses that the transition state involves the accumulation of electron deficiency at the reaction center.

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

(16) A. M. Ward, *J. Chem. Soc.*, 2285 (1927).

(17) A. M. Ward, *ibid.*, 445 (1927).

(18) The various types of substituent constants and their applications have been briefly summarized by C. D. Ritchie and W. F. Sager in "Progress in Physical Organic Chemistry," Vol. 2, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience, New York, N. Y., 1964, pp 323–400.

Activation Parameters.—Table II shows the activation parameters derived from the temperature dependence of the hydrolysis rates in 50% aqueous ethanol. Also included are the calculated rate constants at 25.0°, and the activation parameters for the *p*-methyl derivative, **2a**, in 90% formic acid. Because it was not possible to measure the rates for the *p*-nitro derivative, **2e**, as a function of temperature, data are not available for this substance. The entropies of activation are of particular interest, since they seem to offer evidence that solvent is involved nucleophilically in the transition state. Schalegar and Long have examined the entropies of activation for 23 hydrolysis reactions and have found apparently good correlation between the magnitude of $\Delta S^{\ddagger}$ and whether or not a water molecule is involved in the transition state.[19] In S_N1 and A1 reactions, in which no solvent is thought to be directly involved, the entropies of activation fall in the range of 0 to +10 eu. In S_N2 and A2 reactions, in which a water molecule is involved as a nucleophile, the magnitude of $\Delta S^{\ddagger}$ is from 0 to −30 eu. These ranges seemed to be valid for reactions in aqueous acetone, aqueous ethanol, aqueous dioxane, and water. Additionally, Bordwell and Knipe have shown that for the hydrolysis of α-bromophenylacetate ions, in which the carboxylate anion participates in electrostatic interaction with the reaction center, the magnitude of $\Delta S^{\ddagger}$ is from +11 to +22 eu.[12] The entropies of activation for the present α-chloronitro systems, which range from −3.0 to −8.6 eu, thus seem to accord best with those of reactions involving a nucleophilic push from solvent. Why the $\Delta S^{\ddagger}$ for the *p*-methyl derivative, **2a**, is more negative than that of any other derivative, and why this compound has the same $\Delta S^{\ddagger}$ in both 50% aqueous ethanol and 90% formic acid, are temporary perplexities.

Table II

Activation Parameters for the Hydrolysis of 1-Chloro-1-nitro-1-(*p*-X-phenyl)ethanes[a]

X	E_a kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k, sec^{-1} (25°)
CH_3	24.2	23.6	−8.6	4.371×10^{-7}
H	28.1	27.5	−3.5	7.649×10^{-9}
Cl	28.5	27.9	−3.0	4.697×10^{-9}
Br	27.9	27.3	−5.4	4.078×10^{-9}
CH_3[b]	21.8	21.2	−8.6	2.535×10^{-5}

[a] Hydrolysis in 50% aqueous ethanol containing [$NaClO_4$] of 0.05 mol/l. Rate constants at 25° were obtained by extrapolation using the Arrhenius equation. Activation parameters were calculated at 25°. [b] Hydrolysis in 90% formic acid containing [$NaClO_4$] of 0.065 mol/l.

Reaction Mechanism.—Because of the unexpected facility of these hydrolyses, worthwhile consideration can be given to several mechanistic possibilities. Although free-radical processes appear unlikely, based on previous work with the α-nitrobenzhydryl system,[7] a pathway involving nucleophilic attack on chlorine to give hypochlorous acid and nitronate anion seems plausible at first sight. The reduction of α-halonitro compounds to nitro compounds provides ample precedent for such a reaction course.[20] However, such a scheme is in conflict with the direction of the substituent effects found for the compounds under investigation. Bordwell, Boyle, and Yee have recently shown by measuring the "kinetic acidities" of a series of substituted 1-nitro-1-(X-phenyl)ethanes that substituent effects result in a ρ value of +1.44.[14] In the transition state for this reaction, a proton is being transferred to a hydroxide ion and nitronate anion is being formed. In the present solvolyses, if nucleophilic attack were on chlorine the transition state should resemble electronically that in which a proton is being transferred, and substituent effects in both reactions should be parallel. Since this is not the case, a "positive halogen" type mechanism seems improbable.

An alternative process which involves the initial loss of nitrite ion or nitrous acid to form a chlorocarbonium ion should be considered. Two observations from other systems tend to support the possibility of such a scheme. First, in the α-phenylethyl system, the presence of an α-chloro atom labilizes a leaving group toward ionization by a factor of 32,[21] which suggests that it might be easier to lose the nitro group in these systems than in other nitro compounds. Second, an acid-catalyzed reaction of α-halonitro compounds has recently been reported that clearly involves the loss of nitrous acid to form halocarbonium ion.[22] The reactions reported were carried out either at room temperature with concentrated sulfuric acid or by heating the α-halonitro compound with trichloroacetic acid. The solvolyses reported here are probably mechanistically different from these reactions, based on the apparent lack of influence of acid concentration in the present reactions. During the course of the present runs, the hydronium ion concentration increased because no effort was made to maintain it at a constant value. For example, in one particular run that was followed titrimetrically in 50% ethanol, the pH of the solution went from approximately 7 to less than 2 as the reaction was followed to about 70% completion. No systematic drift was observed in the rate constants calculated from the individual points. On this basis, it seems likely that these solvolyses involve a breaking of the carbon–chlorine bond as the initial process. Although this conclusion seems reasonably well justified for the solvolyses in aqueous ethanol, it may not be valid for the reactions in 90% formic acid.

The lack of a linear correlation for the whole range of substituents in this reaction is reminiscent of the nonlinear Hammett plots obtained for the reactions of a variety of benzylic systems. Such plots are found for the reaction of benzyl chlorides with triethylamine in benzene, of benzyl bromides with pyridine in acetone, of benzyl tosylates in aqueous acetone, aqueous dioxane, and acetic acid, and of α-bromophenylacetate ions in water. Although Hammond and coworkers felt that the nonlinearity reflected a systematic variation of a

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[19] L. L. Schaleger and F. A. Long in "Advances in Physical Organic Chemistry," Vol. 1, V. Gold, Ed., Academic Press, New York, N. Y., 1963, pp 1–31.

[20] (a) M. O. Forster, *J. Chem. Soc.*, **75**, 1141 (1899); (b) M. O. Forster, *ibid.*, **77**, 254 (1900); (c) D. C. Iffland, G. X. Criner, M. Koral, F. J. Lotspeich, Z. B. Papanastassiou, and S. M. White, Jr., *J. Amer. Chem. Soc.*, **75**, 4044 (1953); (d) W. G. Kofron, F. B. Kirby, and C. R. Hauser, *J. Org. Chem.*, **28**, 873 (1963); (e) C. R. Hauser, W. G. Kofron, W. R. Dunnavant, and W. F. Owen, *ibid.*, **26**, 2627 (1961).

[21] J. F. Arens and D. A. van Dorp, *Recl. Trav. Chim. Pays-Bas*, **67**, 973 (1948).

[22] F. Wassmundt, K. B. Galleo, and J. A. Christiano, *Tetrahedron Lett.*, 4311 (1969).

single mechanism,[23] Streitwieser and his coworkers report an abrupt change in mechanism in going from compounds containing activating substituents to those containing deactivating substituents.[24] In support of Streitwieser's interpretation are the results of Gassman and Fentiman.[25] These authors found a linear Hammett correlation over a wide range of substituents for the hydrolysis in 70:30 dioxane–water of 7-aryl-7-norbornyl *p*-nitrobenzoates. With *syn*-7-aryl-*anti*-7-norbornenyl *p*-nitrobenzoates under the same conditions, a sharp break appears in the plot at the point for the *p*-methoxy derivative, and this was interpreted in terms of cessation of neighboring-group participation of the π-electron pair. Here again, the two different ρ values within the series of compounds were interpreted as reflecting two different mechanisms.

It seems likely that the nonlinearity of the Hammett plot for the present data for aqueous ethanol solutions also results from the operation of two mechanism. It should be noted, however, that the limited number of compounds employed in this study precludes stipulation of precisely where the change of slope occurs in the plot. Although it cannot be stated with certainty that the parent compound, for instance, is correctly grouped with the *p*-nitro derivative rather than with the *p*-methyl derivative, visual inspection of the plot suggests that **2b–e** follow one mechanism while **2a** follows another. Speculation concerning the detailed differences between the two is unfortunately premature at this point. It can be observed, however, that the entropies of activation recorded in Table II argue in favor of mechanisms involving the same molecularity. Within the limitations of validity of this argument, a gradation of mechanism, rather than an abrupt change, should perhaps be considered. Because of the paucity of detail afforded by the data, it is assumed for the purpose of discussion that compounds **2b–e** hydrolyze by a mechanism involving a transition state with a lesser degree of carbonium ion character than that for the hydrolysis of **2a**. Further distinction will not be attempted.

Such a mechanistic dichotomy could be attributed to either of two possible phenomena. If compounds **2b–e** require nucleophilic assistance at the reaction center in attaining the transition state, it could be provided either by nitro group participation or by solvent molecules from the solvation sphere. On the basis of very similar findings with respect to ρ values, Bordwell and Knipe,[12] as well as Kemp and Metzger,[11] have argued in favor of carboxylate ion participation in the hydrolysis of α-bromophenylacetate ions substituted with electron-withdrawing substituents. However, the results obtained in 90% formic acid do not substantiate this kind of interpretation for the hydrolysis of the α-halonitro compounds employed in the present investigation. A reasonably good, linear Hammett correlation ($\rho = -3.73$; $r = -0.9951$) is obtained for the hydrolysis of compounds **2a**, **2b**, **2d**, and **2e** (**2c** was not run) in 90% formic acid. It has been pointed out by several authors that ρ is roughly dependent upon the solvent ionizing power, *Y*. Hammond observed a decrease in ρ (to more negative values) for the solvolysis of benzyl tosylates on increasing the water content of aqueous acetone.[23] Bordwell and Knipe have recently made a similar finding for the solvolysis of α-bromo-β-arylpropionates and α,β-dibromo-β-arylpropionates in aqueous ethanol.[13] Data for the hydrolysis of 1-chloro-1-nitro-(*p*-X-phenyl)ethanes also indicate this, as seen by the large decrease in ρ in going from ethanol-water mixtures to 90% formic acid; ρ values are collected in Table III.

TABLE III

VARIATION OF ρ WITH SOLVENT IONIZING POWER IN HYDROLYSIS OF 1-CHLORO-1-NITRO-1-(*p*-X-PHENYL)ETHANES AT 80°

Solvent	*Y*	ρ	*r*
80% Ethanol	0.000	-1.62^a	−0.9959
50% Ethanol	1.655	-1.52^a	−0.9976
90% Formic acid	2.222	-3.73^b	−0.9951

[a] Does not include *p*-methyl derivative. [b] Includes *p*-methyl derivative.

It is interesting to scrutinize the change in ρ in the two solvent mixtures for a possible indication of nitro group participation. Winstein and Heck have suggested that neighboring group participation in solvolysis reactions increases in going to less nucleophilic and more ionizing solvents.[26] If the nitro group is functioning as an internal nucleophile in the hydrolysis of the 1-chloro-1-(*p*-X-phenyl)ethanes, the effect should be more pronounced in 90% formic acid than in the more nucleophilic ethanol–water solvents. The large negative ρ value (−3.73) in 90% formic acid indicates that the incipient benzylic cation in this reaction is very sensitive to substituent effects. If the nitro group is imparting stability to the developing carbonium ion by nucleophilic interaction, a more positive ρ value (less sensitivity to substituent effects) would perhaps be expected.

It is also expected that if nitro group participation is important the extent of such participation should increase as the stability of the incipient benzylic carbonium ion decreases. On this basis the participation should be most important in the *p*-nitro derivative, and consequently the rate should be faster than would be expected from its σ^+ value. The fact that a good correlation exists between log *k* and σ^+ for all the substituents studied indicates that nucleophilic participation by the nitro group is insignificant in the rate-determining step for the hydrolysis of 1-phenyl-1-nitro-1-chloroethanes.

A more plausible interpretation of the finding is as follows. In the more nucleophilic solvents, 50 and 80% ethanol, there is a greater contribution of the direct displacement reaction by solvent for the compounds containing deactivating substituents. In the more ionizing but less nucleophilic solvent, 90% formic acid, a single mechanism with a high degree of carbonium ion character prevails even for the case of the *p*-nitro compound. The slow hydrolysis rate for the *p*-nitro derivative (0.00104, relative to H) in formic acid is indicative of the inability of this substituent to stabilize a positive charge. However, the same mechanism apparently predominates throughout this series of compounds in 90% formic acid and consequently a good correlation with σ^+ obtains. It would perhaps be informative to compare the results of this system with the solvolysis of benzyl tosylates and α-bromophenylacetates in 90% for-

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[23] G. S. Hammond, C. E. Reeder, F. T. Fang, and J. K. Kochi, *J. Amer. Chem. Soc.*, **80**, 568 (1958).

[24] A. Streitwieser, H. A. Hammond, R. H. Jagow, R. M. Williams, R. G. Jesaitis, C. J. Chang, and R. Wolf, *ibid.*, **92**, 5141 (1970).

[25] P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, **92**, 2549 (1970).

[26] S. Winstein and R. Heck, *ibid.*, **78**, 480 (1956).

mic acid. Unfortunately, neither system would be amenable to study in such a solvent.

The possibility of a more dramatic change in mechanism in going to 90% formic acid cannot be ruled out. It is conceivable that in this solvent protonation of the nitro group could occur and loss of nitrous acid to give a chlorocarbonium ion might be the rate-controlling step.

Experimental Section

Melting points were determined on a Büchi melting point apparatus (capillary method) and are uncorrected. Infrared spectra were determined with a Beckman Model IR-8 or a Perkin-Elmer Model 621 grating infrared spectrophotometer. Nuclear magnetic resonance (nmr) spectra were obtained using a Varian Model HA-60 spectrometer with tetramethylsilane as internal reference. Chemical shifts are reported in parts per million (δ) and signals are described as s (singlet), d (doublet), or m (complex multiplet). Ultraviolet and visible spectra were determined using a Cary Model 14 recording spectrophotometer. Elemental analysis was done by M-H-W Laboratories, Garden City, Mich., or by Galbraith Laboratories, Knoxville, Tenn.

1-Nitro-1-(*p*-X-phenyl)ethanes (1a–f).—These compounds were prepared by the method of Bordwell, Boyle, and Yee.[14] Chromatography through 60–100 mesh Florisil using 10:1 petroleum ether[27]–ether eluent, followed by evaporation of solvent, produced these compounds in sufficient purity for elemental analysis. The infrared and nuclear magnetic resonance spectra also accorded with expectation based on the model spectra described.[14]

1-Chloro-1-nitro-1-(*p*-X-phenyl)ethanes (2a–f).—These substances were prepared by the following general procedure.

1-Chloro-1-nitro-1-phenylethane (2b).—Into a 500-ml erlenmeyer flask was placed a solution of 6.83 g (0.045 mol) of 1-phenyl-1-nitroethane in 150 ml of 5% aqueous potassium hydroxide. The flask was cooled to 0° in an ice bath and chlorine was bubbled through the stirred solution for 2 hr. The mixture was extracted twice with 200-ml portions of ether, which were combined, washed with 50 ml of 2 *N* hydrochloric acid and three times with 50-ml portions of water, and dried over magnesium sulfate. Evaporation of the solvent left 7.51 g of a light yellow oil, which was chromatographed on an 18-in. column packed with 60–100 mesh Florisil using petroleum ether (bp 39–60°) as the eluent to give 5.40 g (0.029 mol, 65%) of 1-chloro-1-nitro-1-phenylethane as a light yellow oil: ir (neat) 1560, 1345 (NO_2), 2885, 1460 (CH), 3070, 700 cm^{-1} (ArH); nmr (CCl_4) δ 2.37 (s, 3, CH_3), 7.14–7.60 (m, 5, ArH).

Anal. Calcd for $C_8H_8ClNO_2$: C, 51.72; H, 4.35; N, 7.55; Cl, 19.10. Found: C, 51.64; H, 4.39; N, 7.38; Cl, 19.24.

1-Chloro-1-nitro-1-(*p*-tolyl)ethane (2a).—This substance was obtained in 74% yield, bp 60° (2 × 10^{-4} Torr). Its spectral properties are as follows: ir (neat) 1560, 1330 (NO_2), 3000, 845, 785, 725 (ArH), 2875 cm^{-1} (CH_3); nmr (CCl_4) δ 2.37 (s, 3, CH_3), 2.30 (s, 3, $ArCH_3$, broadened), 6.95–7.44 (2 distorted d, 4, ArH).

Anal. Calcd for $C_9H_{10}ClNO_2$: C, 54.17; H, 5.05; N, 7.02. Found: C, 54.31; H, 5.03; N, 6.83.

1-Chloro-1-nitro-1-(*p*-chlorophenyl)ethane (2c).—This material was prepared in 67% yield. It is a colorless oil: ir (neat) 1559, 1334 (NO_2), 2876, 1383, 1491 (CH_3), 3000, 1596, 751, 825, 848 cm^{-1} (ArH); nmr (CCl_4) δ 2.40 (s, 3, CH_3), 7.12–7.54 (m, 4, ArH).

Anal. Calcd for $C_8H_7NO_2Cl_2$: C, 43.82; H, 3.20; N, 6.35. Found: C, 43.77; H, 3.11; N, 6.12.

1-Chloro-1-nitro-1-(*p*-bromophenyl)ethane (2d).—This compound was produced in 74% yield as a colorless oil: ir (neat) 1563, 1335 (NO_2), 748, 825, 850, 3000 (ArH), 2875, 1383 cm^{-1} (CH_3); nmr (CCl_4) δ 2.42 (s, 3, CH_3), 7.14–7.54 (m, 4, ArH).

Anal. Calcd for $C_8H_7NO_2ClBr$: C, 36.33; H, 2.67; N, 5.30; Br, 30.21; Cl, 13.40. Found: C, 36.58; H, 2.65; N, 5.08; Br, 30.18; Cl, 13.39.

1-Chloro-1-nitro-(*p*-nitrophenyl)ethane (2e).—Crystallization of the crude reaction product from 90% ethanol gave this substance in 46% yield: mp 45°; ir (KBr) 1345, 1560 (NO_2), 690, 720, 860 cm^{-1} (ArH); nmr (CCl_4) δ 2.48 (s, 3, CH_3), 7.64–8.22 (m, 4, ArH).

Anal. Calcd for $C_8H_7N_2O_4Cl$: C, 41.67; H, 3.06; N, 12.15; Cl, 15.37. Found: C, 41.47; H, 3.03; N, 11.96; Cl, 15.60.

1-Chloro-1-nitro-1-(*p*-anisyl)ethane (2f).—This was obtained in 35% yield as a clear, viscous oil: ir (neat) 1560, 1332 (NO_2), 3000, 760, 800, 842, 875 (ArH), 1480, 1390, 2935 cm^{-1} (CH_3). A shift of the nitro group asymmetrical absorption band from 1550 to 1560 cm^{-1}, and in the symmetrical band from 1360 to 1332 cm^{-1}, is evidence of chlorination α to a nitro group. The compound decomposed over a period of hours with the evolution of nitrogen dioxide.

Solutions.—To assure uniformity of solvent composition in all the kinetic runs, stock solutions of the different solvent mixtures were prepared. Aqueous ethanol mixtures of 80, 50, and 40% v/v were prepared by mixing at room temperature the appropriate amounts of commercial 95% ethanol with distilled water. A stock solution of 90% v/v formic acid was similarly prepared by diluting 97% formic acid (Aldrich Chemical Co.) with distilled water. For approximately 1 l. of solution, 927.8 ml of 97% formic acid was mixed with 72.2 ml of distilled water. The formic acid solution for the kinetic runs was made 0.065 *M* in sodium perchlorate by placing 7.959 g (0.065 mol) of anhydrous reagent sodium perchlorate (G. Frederick Smith Chemical Co.) in a 1-l. volumetric flask and diluting to the mark with 90% formic acid. Sodium chloride solutions were prepared by accurately weighing predetermined amounts of the reagent grade material into volumetric flasks and diluting to the mark with the appropriate solvent.

A standard solution of silver nitrate (Baker) was prepared by addition of an accurately weighed amount of silver nitrate (dried at 110° for 1 hr) to a volumetric flask and diluting to the mark with distilled water. Aqueous potassium thiocyanate solutions were prepared by dissolving a preweighed amount of potassium thiocyanate (Fisher White Label) in water and standardizing with standard silver nitrate using a nitric acid solution of ferric ammonium sulfate as the indicator.

Kinetic Measurements.—Kinetics were run in a well-insulated, well-stirred constant-temperature water or mineral oil bath. Temperature control of ±0.05° was accomplished by using a Sargent Model ST Thermonitor. Temperatures were recorded with a thermometer graduated every 0.1°. Elapsed time was recorded using a Precision Scientific Co. clock with a digital read-out in minutes.

Hydrolysis of α-Nitrobenzhydryl Chloride in Aqueous Ethanol.—The kinetics of the solvolysis of α-nitrobenzhydryl chloride were determined by measuring the optical density of the benzophenone produced as a function of time. Freshly sublimed samples of α-nitrobenzhydryl chloride were accurately weighed into 50-ml volumetric flasks and diluted to the mark with stock 80% aqueous ethanol. The final concentrations ranged from 4.138 × 10^{-4} to 7.234 × 10^{-4} mol/l. After vigorous shaking to completely dissolve the α-nitrobenzhydryl chloride, the flasks were immersed in the water bath at the appropriate temperature; 1-ml aliquots were removed at various time intervals and diluted to 10 ml with 95% ethanol. The resulting optical densities were recorded at 252 nm against an ethanol blank. For those runs containing added chloride ion, appropriate quantities of a sodium chloride solution were introduced into the reaction flasks.

To determine the exact initial concentration of α-nitrobenzhydryl chloride, the reactions were allowed to proceed for several half-lives until a constant infinity absorption value was obtained.

Hydrolyris of 1-Chloro-1-nitro-1-(*p*-X-phenyl)ethanes in Aqueous Ethanol.—The extent of solvolysis in aqueous ethanol mixtures of the 1-chloro-1-nitro-1-(*p*-X-phenyl)ethanes, where X = H, Br, Cl, and CH_3, was determined by measuring the optical density of the corresponding acetophenone end products as a function of time. To determine the exact wavelength at which measurements were to be made, commercial samples of the acetophenones were carefully purified and the ultraviolet spectra were recorded in 95% ethanol. Table IV lists the wavelengths

Table IV

Wavelengths and Molar Absorptivities for Para-Substituted Acetophenones

X	λ_{max}, nm	$\epsilon \times 10^{-4}$
H	242	1.52
Br	255	1.71
Cl	252	1.56
CH_3	253	1.47
OCH_3	272	1.59

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(27) Bp 30–60°.

of maximum absorption and the average molar absorptivities for the acetophenones which were determined from several scans at different concentrations.

The 1-chloro-1-nitro-1-(*p*-X-phenyl)ethanes were accurately weighed into 50-ml volumetric flasks and diluted to the mark with the appropriate stock solution of aqueous ethanol. Aliquots of these solutions were transferred to 25-ml volumetric flasks and diluted with the appropriate solvent for the kinetic runs. Runs were made in triplicate and the amount of substrate used was that amount calculated to give a final infinity absorption value between 1.00 and 2.00 OD units. For the runs containing sodium perchlorate or sodium chloride, the desired concentrations were obtained by pipetting aliquots of these salt solutions into the reaction flasks. The flasks were vigorously shaken, stoppered, and placed in the oil or water bath at the desired temperature; 1-ml aliquots were removed with a pipet and diluted to 10 ml with 95% ethanol. The optical densities of these solutions were determined at the appropriate wavelength in matched 1.000 cm cells using 95% ethanol as the blank.

The infinity absorption values were obtained by allowing the reaction to proceed through several half-lives until a constant OD reading was obtained. Calculations were made from the integrated first-order rate expression

$$kt = 2.303 \log [(\mathrm{OD}_\infty - \mathrm{OD}_0)/(\mathrm{OD}_\infty - \mathrm{OD}_t)]$$

where k = first-order rate constant, t = time in seconds, OD_∞ = optical density at infinity time, OD_0 = optical density at zero time, and OD_t = optical density at time t. A plot of log $(\mathrm{OD}_\infty - \mathrm{OD}_t)$ *vs.* t gives a straight line with slope equal to $-k/2.303$. The slopes were calculated from a least-squares computer program.

Hydrolysis of 1-Chloro-1-nitro-1-(*p*-X-phenyl)ethanes in 90% Formic Acid.—Kinetics for these runs could not be followed spectrophotometrically because of solvent cut-off in the range of interest due to the high concentration of formic acid. The rates were followed instead by measuring the amount of chloride ion released by the reaction as a function of time. The Volhard titrimetric procedure was employed.[28]

Samples of the 1-chloro-1-nitro-1-(*p*-X-phenyl)ethanes sufficient to give a final concentration of approximately 3.0×10^{-2} mol/l. were accurately weighed into 25-ml volumetric flasks and diluted to the mark with stock 90% formic acid containing 0.065 mol/l. of sodium perchlorate. The flasks were shaken until dissolution of the substrate was complete and were then immersed in an oil or water bath at the desired temperature; 2-ml aliquots were removed at various time intervals and pipetted into 5 ml of water contained in a 50-ml erlenmeyer flask.

A known excess of standard silver nitrate solution was added to the flask, followed by 2 ml of dilute nitric acid, 1 ml of a saturated solution of ferric ammonium sulfate in dilute nitric acid, and 1 ml of nitrobenzene. The mixture was vigorously agitated with a magnetic stirrer and the excess silver nitrate was back titrated to the rusty-red end point with standard potassium thiocyanate.

Calculations were made from the integrated first-order rate expression

$$k = (2.303/t) \log [a/(a - x)]$$

where k = first-order rate constant, t = time in seconds, a = initial quantity of substrate in given volume, x = amount of substrate reacting in time t, and $a - x$ = amount of substrate remaining at time t. A plot of log $[a/(a - x)]$ *vs.* t gives a straight line with slope equal to $k/2.303$.

Activation Parameters.—Activation parameters were calculated by least-squares programs utilizing the Arrhenius and absolute rate equations.

Registry No.—**2a,** 31659-47-9; **2b,** 31657-66-6; **2c,** 31657-67-7; **2d,** 31657-68-8; **2e,** 31657-69-9; **2f,** 31657-70-2.

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Chlorination of Alkenes with Trichloramine[1]

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Trichloramine in nonpolar solvent gave excellent yields of vicinal dichlorides with certain types of olefins. Nitrogen was generated almost quantitatively, along with the by-products, ammonium chloride and basic material. With 1-hexene, 1-octene, cyclopentene, cyclohexene, 3-chloropropene, and 1,1-dichloroethylene as substrates, yields of the corresponding *vic*-dichlorides ranged from 89 to 97%. The *meso*:*dl* ratios for chlorination of the isomeric 2-butenes were similar to those obtained from molecular chlorine under radical conditions. Additional evidence for a radical mechanism was derived from relative reactivities, catalysis, formation of some *cis*-1,2-dichlorocyclohexane from cyclocyclohexene, and participation of an alkane additive. The high addition:substitution ratios suggest that free chlorine atoms are generated in no more than minor amounts. The detailed aspects of the radical pathway are discussed.

The most pertinent prior reference describes the formation of 1,2-dichlorocyclohexane in 77% yield from cyclohexene and trichloramine.[3] However, there has been no follow-up of this work since it appeared more than 40 years ago.

The bulk of the previous investigations involving the interaction of *N*-chloramines with olefins involves the chloramination reaction. Only a brief summary will be presented since a review of the subject is available elsewhere.[4] Coleman and coworkers revealed that trichloramine underwent addition to various olefins, *e.g.*, ethylene, isobutylene, cyclohexene, and styrene.[5-7] *N*,*N*-Dichloro-β-chloroalkylamines were postulated as the initial adducts which were converted to β-chloroalkylamines, <20%, after work-up with concentrated hydrochloric acid. Unspecified amounts of dichloride, along with nitrogen and ammonium chloride, were also obtained. Unsymmetrical olefins formed β-chloroalkylamines in which chlorine was affixed to the least substituted olefinic carbon atom. Under photolytic or thermal conditions chloramine gave low yields of *vic*-dichlorides with simple olefins.[8,9] *N*-Halo-1,2,4-

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